Argonne National Laboratory

A TREATMENT OF SOME
PERIODIC POTENTIAL PROBLEMS

by

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ABSTRACT

A new method of treating periodic potential problems which has
some pedagogical interest and appears to offer some simplifications
is described. The classical Kronig-Penny problem is treated as an
introduction to the applications after which the method is used to
obtain the band structure for the periodic potential, the "parabolic
scallop potential", consisting of a linear chain of segments of
vertical parabolas opening upwards. The general problem for the one-
dimensional periodic potential with reflection symmetry is then
treated and illustrated by application of the method to the linear
chain of inverted parabolic segments. As a third example the band
structure is obtained for the "hip-roof" potential. Finally, the
three-dimensional problem is discussed.

1. Introduction

In the following discussion we consider Schroedinger problems

involving the motion of a single particle in an infinitely periodic

potential. Thus

$$V(\bar{r} + \bar{l}) = V(\bar{r}) \qquad , \qquad (1)$$

where $V(\bar{r})$ is a real potential involving only the spatial coordinates,

$\bar{r} \equiv (x,y,z)$; i.e. $V(\bar{r})$ is a scalar point function, and $\bar{l}$ is any

vector joining equivalent points of a three-dimensional periodic

structure. The appropriate steady state Schroedinger equation for

these periodic potential problems is,

$$- \frac{\hbar^2}{2m} \nabla^2 \psi + [V(\bar{r}) - E] \psi = 0 \qquad , \qquad (2)$$

where $\psi \equiv \psi(\bar{r})$ is the eigenfunction for the state of the system of

total energy E and $V(\bar{r})$ is the periodic potential. To complete the

solution of the problem, one must select from all of the functions $\psi(\bar{r},E)$ which satisfy equation (2), those solutions which according to accepted quantum mechanical principles have certain "well-behaved" properties. For quantum mechanical systems such well-behaved solutions $\psi(\bar{r},E)$ do not exist for all values of E. On the contrary, well-behaved solutions exist in general only for discrete energy levels or for bands of energy in the case of periodic potentials.

2. Criteria for the Selection of Proper Functions

The proper criterion for the selection of the appropriately "well behaved" (physically useful) solutions, $\psi(\bar{r},E)$, of equation (2), where $V(\bar{r})$ is periodic, has been pointed out by Bloch[1] in an important theorem. The statement of this theorem is as follows:

Theorem I. The physically useful solutions of the Schroedinger equation with a periodic potential are of the form

$$\psi_k(\bar{r}) = u_k(\bar{r}) \; e^{i\bar{k}\cdot\bar{r}} \quad , \tag{3}$$

where $u_k(\bar{r})$ is a function which is periodic in x,y,z with the periodicity of the lattice, and depends in general on the real wave vector $\bar{k}$.

The solutions (3) are known as Bloch functions. The allowed energies are determined by them. The unwanted or "ill-behaved" solutions not belonging to the set (3) go to infinity at $\bar{r}(x,y,z) = \infty$ in an exponential way.[2] Such unbounded solutions do not allow the calculation

[1] F. Bloch, Z. Physik, 52, 555 (1928).

[2] A. H. Wilson, "The Theory of Metals", Cambridge Press (1953), pp. 21-25.

of quantum mechanical averages of operators which correspond to physically observable quantities.

According to the Born interpretation, the value of the square of the modulus of an eigenfunction, $|\psi(\bar{r})|^2$, measures the particle's position probability density. Accepting this interpretation, it seems clear from a strictly physical point of view that the probability density for a steady state must be the same at all points of a periodic lattice which are equivalent with respect to the operation of translation. This gives rise to the following theorem:

> Theorem II. Any physically suitable solution $\psi(\bar{r},E)$
> of equation (2), where $V(\bar{r})$ is a periodic potential,
> must satisfy the relation
>
> $$|\psi(\bar{r} + \mathcal{l})|^2 = |\psi(\bar{r})|^2 \quad , \tag{4}$$
>
> where $\mathcal{l}$ is any lattice vector joining equivalent
> points of the periodic structure.

Theorem II furnishes a somewhat more physically satisfying criterion for the selection of the appropriate solutions of (2). It is obvious that if $\psi(\bar{r},E)$ obeys equation (3), it also obeys (4). Hence, Theorem II is a corollary of Theorem I and equation (4) is a necessary condition for physically acceptable solutions. We show in later discussion that (4) is also a sufficient condition for one-dimensional problems. However, for three dimensional problems, we need an additional criterion.

In addition to the physically interpretable position probability density $|\psi(r,E)|^2$ of quantum mechanics, there is a second quantity determined from the eigenfunctions which behaves mathematically in an analogous way to the classical current density of fluid flow. This quantity is called the probability current density $\bar{S}(\bar{r},t)$.[3] Its

definition in terms of the eigenfunctions is

$$\bar{S}(\bar{r},t) = \frac{\hbar}{2im} \left\{ \psi^* \nabla \psi - \psi \nabla \psi^* \right\} \quad , \tag{5}$$

where the asterisk indicates the complex conjugate quantity and the bar over S denotes its vector nature. One can easily show from the differential equation (2) that the time independent $\bar{S}(\bar{r})$ is divergenceless. That is, all steady state solutions, whether physically acceptable or not, satisfy the relation:

$$\nabla \cdot \bar{S}(\bar{r}) = 0 \quad . \tag{6}$$

The Bloch functions (3) satisfy (6), by virtue of being solutions of (2). However, the Bloch functions are restricted to those solutions which make the probability current density periodic with the periodicities of the lattice. Thus

$$\psi = u(\bar{r})\, e^{i\bar{k}\cdot\bar{r}} \;\; ; \;\; u(\bar{r} + \bar{l}) = u(\bar{r}) \quad ,$$

$$\nabla\psi = (\nabla u + i\bar{k}u)\, e^{i\bar{k}\cdot\bar{r}} \quad ,$$

$$\nabla\psi^* = (\nabla u^* - i\bar{k}u^*)\, e^{-i\bar{k}\cdot\bar{r}} \quad , \tag{7}$$

$$\psi^* = u^*\, e^{-i\bar{k}\cdot\bar{r}} \quad ,$$

$$S = \frac{\hbar}{2im}\, [u^*\nabla u + 2i\bar{k}uu^* - u\nabla u^*] \quad .$$

Hence

$$\bar{S}(\bar{r} + \bar{l}) = \bar{S}(\bar{r}) \quad . \tag{8}$$

Equation (8) automatically holds for one-dimensional problems,[*] and presents no additional selection criterion beyond that of equation (4) for physically acceptable solutions. However, it does give a further restriction over equation (4) for three dimensional

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[3]See for example, "Quantum Mechanics" by Leonard Schiff, p.23, McGraw-Hill Book Company, Inc. (1949).

[*]$\nabla \cdot \bar{S} = 0 \rightarrow \dfrac{\partial S}{\partial x} = 0 \; ; \; S = \text{constant}.$

problems. The physical basis for the criterion (8) is not as clear as the basis for (4), although the analogy of the quantum mechanical probability current density $\bar{S}(\bar{r})$ to classical flow densities certainly makes criterion (8) appear reasonable. In any case, in Appendix I, we prove the complete equivalence of the Bloch criteria and the two criteria (4) and (8) for physically acceptable solutions. These alternate criteria are repeated in the following theorem:

> Theorem III. The physically suitable solutions
> $\psi(\bar{r},E)$ of equation (2), where $V(\bar{r})$ is a periodic potential,
> are those and only those solutions which satisfy the
> following two relations:
>
> $$|\psi(\bar{r} + \bar{l})|^2 = |\psi(\bar{r})|^2 \qquad , \qquad (4)$$
>
> $$\bar{S}(\bar{r} + \bar{l}) = \bar{S}(\bar{r}) \qquad , \qquad (8)$$
>
> where $\bar{l}$ is any lattice vector joining equivalent points
> of the periodic structure.

Thus, (4) and (8) are both necessary and sufficient conditions for the eigenfunctions to obey the Bloch criteria; we may use either equations (4) and (8) or alternately (3) for the selection of physically suitable eigenfunctions for the periodic potential problem.

3. One-Dimensional Problems - Periodic Potential - Even Potential

Let us consider one-dimensional periodic potential problems for which $V(x)$ is an even function about some lattice point and about every equivalent point. We choose this set of symmetry points for convenience to be $0, \pm l, \pm 2l, \ldots$ Hence we now have

$$\frac{-\hbar^2}{2m} \psi''(x) + \left\{V(x) - E\right\} \psi(x) = 0 \quad , \tag{9}$$

$$V(x + \ell) = V(x) \quad , \tag{10}$$

and

$$V(x) = V(-x) \quad . \tag{11}$$

This further restriction on $V(x)$ is not very limiting since practically all physically interesting potentials will have reflection symmetry.

From the physically intuitive point of view, it might seem quite reasonable to expect that the position probability density for a physically acceptable steady state solution would have the same values at equal distances on opposite sides of reflection symmetry points. In other words, one might expect that for $V(x) = V(-x)$, we would also have

$$|\psi(-x)|^2 = |\psi(x)|^2 \quad , \tag{12}$$

since the system has no way of making a preferential decision with respect to the probability of being at these equivalent points. In this connection we prove in Appendix II the following theorem:

> Theorem IV. Physically acceptable solutions of the
> infinitely periodic potential problem obeying the
> Bloch conditions (3) or the periodicity condition
> on the probability density (4) also obey the evenness
> relation
> $$|\psi(x)|^2 = |\psi(-x)|^2 \quad , \tag{13}$$
> when $V(x)$ is an even function about $x = 0$.

Actually, as pointed out in Appendix II, an exception to Theorem IV can arise if both a symmetric and an antisymmetric solution exists for the same eigenvalue such that both are periodic or both antiperiodic. Thus, if ψ_1 and ψ_2 are the antisymmetric and symmetric solutions for the eigenvalue E, we have, for $\alpha = \pm 1$,

$$\psi_1(x + \ell) = \alpha\psi_1(x) \qquad , \qquad (14a)$$

$$\psi_2(x + \ell) = \alpha\psi_2(x) \qquad , \qquad (14b)$$

$$\psi(x) = A\psi_1(x) + B\psi_2(x) \qquad , \qquad (14c)$$

$$\psi(x + \ell) = \alpha\psi(x) \qquad , \qquad (14d)$$

$$|\psi(x + \ell)|^2 = |\psi(x)|^2 \qquad , \qquad (14e)$$

$$|\psi(-x)|^2 \neq |\psi(x)|^2 \qquad . \qquad (14f)$$

The last inequality holds if A and B are completely arbitrary. An equality arises if $AB^* + A^*B = 0$.

Wilson[2] points out that the periodic and antiperiodic solutions are just the solutions which separate the allowed and the forbidden bands. Hence the above exception, if it exists, occurs on the edge of a band, whereas <u>within</u> an allowed band the relation $|\psi(x)|^2 = |\psi(-x)|^2$ is certainly valid. On the edge of a band the relation is also obeyed for those periodic and antiperiodic solutions which are <u>either</u> purely symmetric <u>or</u> purely antisymmetric [and in addition for those solutions of mixed symmetry which have the form $\psi(x) = a\psi_1(x) \pm ib\psi_2(x)$ since $AB^* + A^*B = 0$ for those cases also.] If there is no relation on the phases of the coefficients in equation (14c), then an exception could arise to the reflection symmetry property of $|\psi(x)|^2$. This

might take place, for example, if two bands were to touch or cross
for some value of the parameters (lattice period, etc.) of $V(x)$.
Thus, for example, a lower level of odd symmetry of an adjacent
higher band and an upper level of even symmetry of the lower band
might move together for some value of the lattice parameter giving
a double degeneracy. In any case, since A and B are perfectly
arbitrary, no energy structure would be lost by choosing $AB^* + A^*B = 0$,
thereby removing the exception to Theorem IV. Further discussion
regarding the symmetries of the eigenfunctions at the band edges
will be deferred until the applications are described.

4. Properties of the Logarithmic Derivative -- One-Dimensional
   Periodic Potential Problems

The problems we wish to solve are subject to the following
set of conditions:

$$-\frac{\hbar^2}{2m} \psi'' + \left\{ V(x) - E \right\} \psi = 0 \qquad , \qquad (15a)$$

$$V(x) \text{ is real} \qquad , \qquad (15b)$$

$$V(x + \ell) = V(x) \qquad . \qquad (15c)$$

Because of the condition (15c) - a periodic structure - we have
seen that the position probability density is periodic. Furthermore,
the probability current density $S(x)$ is constant, hence periodic,
for these one-dimensional problems. Therefore

$$S = \frac{\hbar}{2im} \left(\psi^* \frac{d\psi}{dx} - \psi \frac{d\psi^*}{dx} \right) \qquad , \qquad (16)$$

is the same for all values of $\underline{x}$, for a given $\psi(x, E)$, and furthermore
S is real since it is the sum of complex conjugates. Let us divide
equation (16) through by $\psi^*(x) \cdot \psi(x)$, an operation valid except where

$\psi(x)$ vanishes. [If $\psi(x_o) = 0$ at some point x_o then by (16) $S(x_o) = 0$ which requires $S(x) \equiv 0$ and $\frac{S}{|\psi|^2} = 0$.] Thus, we have

$$\frac{S}{\psi\psi^*} = \frac{\hbar}{2im} \left(\frac{1}{\psi} \frac{d\psi}{dx} - \frac{1}{\psi^*} \frac{d\psi^*}{dx}\right) \qquad . \qquad (17)$$

Also,

$$\frac{1}{\psi\psi^*} \frac{d}{dx} (\psi\psi^*) = \left(\frac{1}{\psi} \frac{d\psi}{dx} + \frac{1}{\psi^*} \frac{d\psi^*}{dx}\right) \qquad . \qquad (18)$$

It follows from these equations that

$$\frac{1}{\psi} \frac{d\psi}{dx} = \frac{1}{2} \frac{1}{|\psi|^2} \frac{d|\psi|^2}{dx} + \frac{im}{\hbar} \frac{S}{|\psi|^2} \qquad . \qquad (19)$$

Since $|\psi|^2$ and its derivative are periodic with period ℓ, $\frac{1}{\psi} \frac{d\psi}{dx}$ is also periodic with period ℓ. Let us set

$$\frac{1}{\psi} \frac{d\psi}{dx} = P = P_R + iP_I \qquad . \qquad (20)$$

Both P_R and P_I are real periodic functions of period ℓ.

It is clear from (20) that the imaginary part of P is related to S:

$$S = \frac{\hbar}{m} P_I |\psi|^2 \qquad . \qquad (21)$$

Since $|\psi|^2$ has the units of number of particles per unit volume and S has the units of particle flux, particles/cm^{2}sec, $\hbar P_I/m$ must have the units of velocity and, therefore, P_I has the units of momentum.

From the definition of $P(x)$ in (20) and the Schroedinger equation, we obtain the following equation:

$$P' + P^2 + \frac{2m}{\hbar^2} (E - V) = 0 \qquad . \qquad (22)$$

Thus, the second-order linear Schroedinger equation has been replaced by a first order second degree equation of the standard Ricatti form. If one has a particular solution of (22) then the general solution can be found by simple quadrature.

Our problem now is to find solutions of (22) in the interval $-\frac{\ell}{2} \leqslant x \leqslant \frac{\ell}{2}$, or some equivalent interval, which can be "joined" to identical solutions in adjacent cells to form a periodic P(x). After this has been done, the eigenfunctions can be obtained by quadrature of (20).

For example, if $P_I(x)$ is not identically zero, then we have

$$P_I = \frac{mS}{\hbar |\psi|^2} , \tag{23}$$

and since S = constant,

$$P_R = \frac{1}{2|\psi|^2} \frac{d|\psi|^2}{dx} = -\frac{1}{2P_I} \frac{dP_I}{dx} , \tag{24}$$

from which it follows from (19) that

$$\ell n\psi = -\frac{1}{2} \ell nP_I(x) + i\int P_I \, dx + C , \tag{25}$$

$$\psi = \psi(a)\sqrt{\frac{P_I(a)}{P_I(x)}} \; e^{i\int_a^x P_I \, dx} . \tag{26}$$

We know also that in this case $\psi(x)$ cannot become zero at any point, for if it did, then by equation (16), S ≡ 0, and $P_I(x)$ ≡ 0 contrary to assumption. Hence we conclude from (23) that $P_I(x)$ can never be infinite. Furthermore, if $P_I(x)$ = zero at some point x then by (23) either S = 0 at that point, and consequently everywhere, from which P_I ≡ 0, or $\psi(x)$ goes to infinity in accordance with (26). Obviously, we must restrict our solutions of P and hence of P_I such that infinities of $\psi(x)$ either do not occur or if they do, that they be such that one can calculate the probability of finding the particle in a finite interval including the infinite point of $\psi(x)$. That is

$$\int_{x_o-a}^{x_o+a} |\psi(x)|^2 \, dx = \text{finite value} \tag{27}$$

for <u>a</u> finite even if $\psi(x_o) \to \infty$.

If $P_I(x) \equiv 0$ in our solution, then $\psi(x)$ is given by:

$$\frac{1}{\psi} \frac{d\psi}{dx} = P_R \ , \tag{28a}$$

$$\psi = Ae^{\displaystyle \int_a^x P_R(x) \, dx} \ , \tag{28b}$$

where A is arbitrary and can be chosen real. Hence $\psi(x)$ can be taken to be a real function.

It is useful to compare (26) and (28b) with the Bloch functions. Since P is periodic, then both P_R and P_I are periodic. The integral $\int P_I \, dx$ will give, in general, $a_o x + a$ periodic function -- as can be seen easily by thinking of the Fourier series development of $P_I(x)$. ($P_I(x)$ is never infinite!) The periodic part can be combined with the periodic pre-exponential $1/\sqrt{P_I(x)}$ in equation (26) to give a Bloch periodic u(x) and a Bloch $\underline{k} = a_o$.

In the case where $P_I(x) \equiv 0$, $P(x) = P_R(x)$ is real and periodic. However, contrary to $P_I(x)$, $P_R(x)$ is not confined to finite and continuous functions. Being periodic $P_R(x)$ must have <u>an even number of changes in sign in a lattice period.</u> These changes in sign can be of the regular variety in which $P_R(x)$ goes through zero in a continuous way corresponding to $\psi'(x_o) = 0$ for $x \to x_o$. (See equation (28a.).) Or $P_R(x)$ can change sign in a discontinuous way jumping from $-\infty$ to $+\infty$ as x goes through x_o. This latter behavior leads to $\psi(x_o) = 0$ as can be seen from equation (28b). Jumps of $P_R(x)$ from a finite negative value to a finite positive value at some point x_o cannot take place, for this would lead to a non-zero $\psi(x_o-)$ and an equal

non-zero $\psi(x_o+)$ as limits for $\psi(x)$ as $x \to x_o$ from the left and right. However, the non-zero ψ' limits for $\psi'(x)$, $\psi'(x_o-)$ and $\psi'(x_o+)$, would not be equal. (See equations (28a) and (28b).) This would mean that $\frac{d}{dx} |\psi|^2 = 2\psi'\psi$ (ψ is real) is not continuous across x_o. Such a situation is contrary to the continuity conditions of quantum mechanics (p. 29 of ref. 3) which require both $\psi(x)$ and $\psi'(x)$ to be continuous across any point x_o lying in an interval in which $V(x)$ is finite. If $V(x)$ is infinite at x_o, then $\psi(x_o) = 0$ and $\frac{d|\psi|^2}{dx}$ also matches across x_o. [As will be seen in the next section, the requirement of the continuity of $\frac{d|\psi|^2}{dx}$, $\nabla|\psi|^2$ for three-dimensional motion, is somewhat less restrictive than the conventional matching conditions. However, the less restrictive condition leads to nothing new which is physically observable.] We conclude therefore that jumps in $P_R(x)$, if they occur, are infinite in nature. Hence for these cases, the Fourier series development of $P_R(x)$ cannot be carried out. Nevertheless, we can easily see from the behavior of $P_R(x)$ what the equivalent Bloch k will be. Changes in sign of $P_R(x)$ taking place by the continuous process do not lead to a change in sign of $\psi(x)$ but changes in sign of $P_R(x)$ by the discontinuous process do lead to a change in sign of $\psi(x)$. In fact, one can easily convince himself that if the discontinuous variety occurs, they must alternate with the continuous variety. Since $\psi(x)$ is real, the periodicity of $|\psi(x)|^2$ leads to $k = 0$ for $P_R(x)$ continuous and $k = 0$ for an even number of discontinuous changes in $P_R(x)$ and $k = \pm \frac{\pi}{\ell}$ for an odd number of discontinuous changes in sign per period of $P_R(x)$. These are the only Bloch k values allowed.

5. Matching Conditions at Discontinuities in the Potential Function

Consider a potential function which has a finite point discontinuity illustrated in Figure 1.
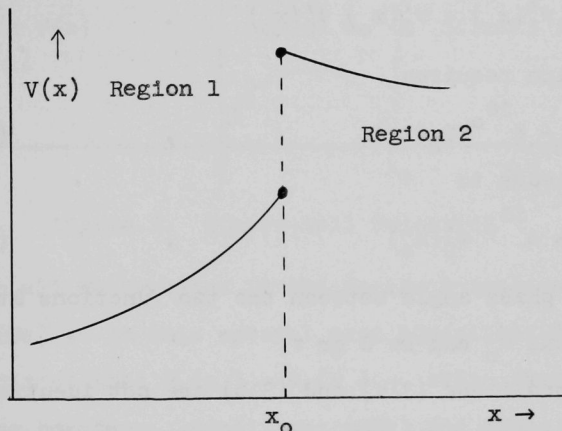
Figure 1. Discontinuous Potential

It is customary to require $\psi(x)$ and $\psi'(x)$ to match separately across the discontinuity. Such matching conditions will certainly insure the matching of the following physical quantities

$$\psi(x) \, \psi^*(x) = |\psi(x)|^2 \qquad , \qquad (29a)$$

$$S = \frac{\hbar}{2im} \left(\psi^*\frac{d\psi}{dx} - \psi\frac{d\psi^*}{dx}\right) \qquad , \qquad (29b)$$

$$\frac{d(\psi\psi^*)}{dx} = \psi^*\frac{d\psi}{dx} + \psi\frac{d\psi^*}{dx} \qquad . \qquad (29c)$$

With these matched, we see from (19) that $P = (P_R, P_I)$ is also matched. From the physical intuition point of view, it would seem equally reasonable to take as the quantities to be matched just (29a, b, and c). Equivalent to the matching of (29a, b, and c) is the requirement that $P = (P_R, P_I)$ and $|\psi(x)|^2$ match across a discontinuity.

By combining the matching of (29b) and (29c) one finds that $\psi^*(x) \cdot \psi'(x)$ must match. Thus, we have

$$\psi_1(x_o) \; \psi_1^*(x_o) = \psi_2(x_o) \; \psi_2^*(x_o) \qquad , \qquad (30a)$$

$$\psi_1'(x_o) \; \psi_1^*(x_o) = \psi_2'(x_o) \; \psi_2^*(x_o) \qquad . \qquad (30b)$$

The first equation requires

$$\psi_1(x_o) = e^{i\theta_o} \; \psi_2(x_o) \qquad , \qquad (31a)$$

and the second leads to

$$\psi_1'(x_o) = e^{i\theta_o} \; \psi_2'(x_o) \qquad , \qquad (31b)$$

where θ_o is the phase angle between the two functions at x_o. For real functions θ_o can be 0 or π!

Although conditions (31a) and (31b) are not identical to the usual matching requirements, they do not give rise to any physically different results than those obtained by choosing $\theta_o = 0$. We can easily see that this is so with respect to the energy. Thus inside Region 2, Figure 1, where $V(x)$ is continuous, the eigenfunction $\psi_2(x)$ is determined through the Schroedinger equation by the initial values at (x_o+) of $\psi_1(x_o)e^{-i\theta_o}$ and $\psi_1'(x_o)e^{-i\theta_o}$. But these are both just $e^{-i\theta_o}$ times their values with $\theta_o = 0$; hence the eigenfunction throughout Region 2 is $e^{-i\theta_o}$ times the value it would have with the conventional matching conditions (because of the linearity of the Schroedinger equation). No curvatures, $\frac{\psi''(x)}{\psi(x)}$, have been changed; hence the energy is unchanged.

Actually our statement of the appropriate matching conditions holds also for infinite discontinuities. Consider for example, the infinitely deep and completely isolated "square-well" potential. See Figure 2. In this case it is obvious that $\psi(x)$ vanishes

Region 2
Infinite V(x)

Region 1
V(x) = 0

Region 2
Infinite V(x)

0   x_0 $\rightarrow x$
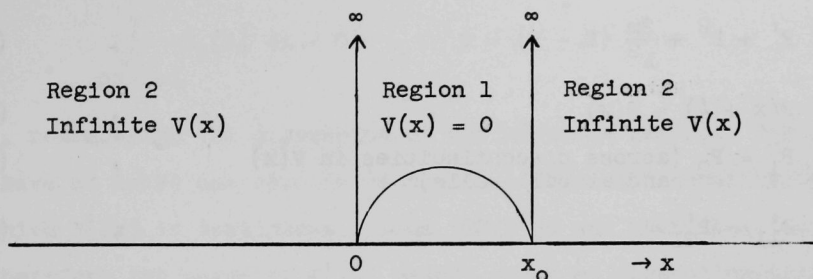
Figure 2. Square-Well Potential

identically in all derivatives in the Region 2 outside the well.
Matching of (29a) -- in this special case equivalent to the
customary condition that $\psi_1(x_0) = \psi_2(x_0)$ -- shows that $\psi_1(x)$
vanishes on the boundary. Conditions (29b) and (29c) are now
automatically satisfied, <u>independent of the value $\psi_1'(x_0)$</u>, which
certainly cannot be zero if $\psi(x)$ is not to vanish identically.

The above matching conditions are perfectly general. They
apply for non-periodic potential problems as well as for periodic ones
and they are also the proper conditions to use for the "joining"
of P(x) at the cell boundaries whether V(x) is continuous and
smooth or not.

Finally, it is worth pointing out that for discontinuous
"jumps" in potential, P(x) must match but P'(x) will not as is
easily seen from equation (22). In fact $P_I'(x)$ matches but
$P_R'(x)$ does not. However, even if V is not smooth - but is
continuous - for example as at a cusp - P'(x) matches.

6. Summary of the Properties of $P_R(x)$ and $P_I(x)$ - Even Potentials

$$P = P_R + iP_I = \frac{1}{2|\psi|^2} \frac{d|\psi|^2}{dx} + i \frac{m}{\hbar} \frac{S}{|\psi|^2} \qquad , \qquad (32a)$$

$$P' + P^2 + \frac{2m}{\hbar^2}(E - V) = 0 \qquad , \qquad (32b)$$

$$P(x + \ell) = P(x) \qquad , \qquad (32c)$$

$$P_1 = P_2 \quad \text{(across discontinuities in } V(x) \text{ and at cell walls)} \qquad , \qquad (32d)$$

$$P'_{1I} = P'_{2I} \qquad , \qquad (32e)$$

$$P'_{1R} \neq P'_{2R} \; ; \; \Delta P'_R = \frac{2m}{\hbar^2} \Delta V \qquad . \qquad (32f)$$

Since $|\psi(x)|^2 = |\psi(-x)|^2$ inside the allowed bands, we have from (32a) the important symmetry results:

$$P_I(-x) = P_I(x) \qquad , \qquad (33a)$$

$$P_R(-x) = -P_R(x) \qquad . \qquad (33b)$$

Also when $P_I(x) \neq 0$, $\psi(x)$ is never zero, and $P_R(x)$ is never infinite, but must have zeros - of the ordinary variety - for otherwise $\frac{dP_I}{dx}$ could not be zero and hence P_I could not be periodic except for the trivial free particle case of $P_I \equiv K$, $P_R \equiv 0$. Hence for $P_I(x) \neq 0$, $P_R(x)$ is a well-behaved antisymmetric periodic function.

The eigenfunctions are given by

$$\psi(x) = \psi(a) \sqrt{\frac{P_I(a)}{P_I(x)}} \; e^{i \int_a^x P_I \, dx} \qquad , \qquad (33c)$$

or by,

$$\psi(x) = \psi(a) \; e^{\int_a^x P_R \, dx} \qquad , \qquad (33d)$$

according to whether $P_I(x) \neq 0$ or vanishes identically.

If $P_I(x)$ vanishes, we also have

$$|\psi(x + \ell)|^2 = |\psi(o)|^2 \; e^{2 \int_o^{x+\ell} P_R(x) \, dx} =$$

$$|\psi(x)|^2 = |\psi(o)|^2 \; e^{2 \int_o^x P_I(x) \, dx}$$

Hence
$$e^{2\int_{x}^{x+\ell} P_R(x)\, dx} = 1 \quad ,$$

and
$$\int_{period} P_R(x)\, dx = 0 \quad . \tag{33e}$$

Hence, remembering the discussion of the previous section, $P(x) = P_R(x)$ must have at least one zero in each cell of the continuous variety and for which $P_R'(x)$ is continuous. From (32f) we see that these zeros and therefore the zeros of $\psi'(x)$ cannot occur at <u>discontinuities</u> in the potential.

We will now proceed to the actual solution of a number of examples of periodic potential problems using the above described matching conditions and the periodicity on P. In a sense the most difficult and least rewarding example is the "classic" Kronig-Penny problem. However, it is the standard textbook example and will be treated first.

7. <u>Kronig-Penny Periodic Potential</u>. See Figure 3.
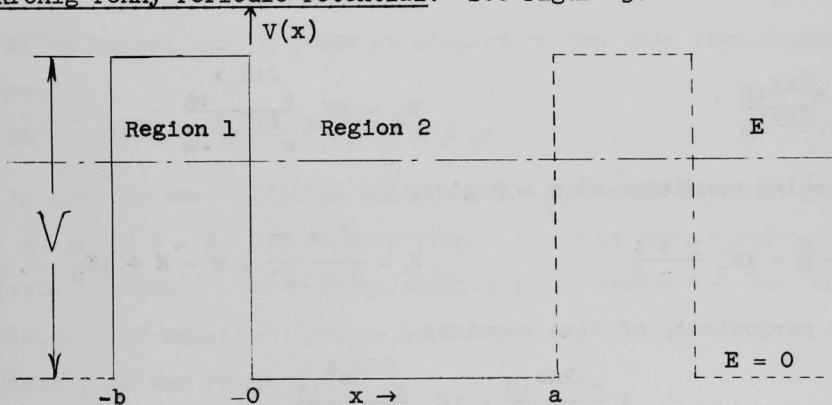
Figure 3. Kronig-Penny Potential

We proceed with the solutions as follows:

Region 1.

$$P' + P^2 + \frac{2m}{\hbar^2}(E - V) = 0 \quad ; \qquad$$

Region 2.

$$P' + P^2 + \frac{2m}{\hbar^2}E = 0 \qquad , \quad (35a)$$

$$P' + P^2 - K^2 = 0 \qquad ; \qquad P' + P^2 + K_0^2 = 0 \qquad , \quad (35b)$$

$$K^2 = \frac{2m}{\hbar^2}(V - E) \qquad ; \qquad K_0^2 = \frac{2mE}{\hbar^2} \qquad , \quad (35c)$$

particular solution $= - K$;   particular solution $= - iK_0$,

general solution:

$$P_1 = - K + \frac{e^{2Kx}}{I + C_1} \qquad ; \qquad P_2 = - iK_0 + \frac{e^{2iK_0 x}}{J + C_2} \qquad ,$$

$$I = \int_0^x e^{2Kx}dx = \frac{e^{2Kx}-1}{2K} \qquad ; \qquad J = \int_0^x e^{2iK_0 x}dx = \frac{e^{2iK_0 x}-1}{2iK_0} \qquad ,$$

$$1 - 2KC_1 = B \qquad ; \qquad 1 - 2iK_0 C_2 = A \qquad ,$$

$$P_1 = - K + \frac{2Ke^{2Kx}}{e^{2Kx}-B} \qquad ; \qquad P_2 = - iK_0 + \frac{2iK_0 e^{2iK_0 x}}{e^{2iK_0 x}-A} \qquad , \quad (36a)$$

$$P_1 = K \frac{e^{2Kx}+B}{e^{2Kx}-B} \qquad ; \qquad P_2 = iK_0 \frac{e^{2iK_0 x}+A}{e^{2iK_0 x}-A} \qquad . \quad (36b)$$

The matching condition at $x = 0$ gives

$$K \frac{1 + B}{1 - B} = iK_0 \frac{1 + A}{1 - A} \qquad , \qquad A = \frac{q^* + Bq}{q + Bq^*} , \quad q = K + iK_0 \qquad , \quad (37a)$$

and the periodicity of $P(x)$ requires

$$K \frac{e^{-2Kb}+B}{e^{-2Kb}-B} = iK_0 \frac{e^{2iK_0 a}+A}{e^{2iK_0 a}-A} \qquad . \quad (37b)$$

We now eliminate A from (37a) and (37b) obtaining the following quadratic equation on B:

$$e^{Kb}B^2(K^2+K_o^2)\sin K_o a + B[(K^2-K_o^2)2\sin K_o a \cosh Kb + 4K_o K \cos K_o a \sinh Kb]$$

$$+ e^{-Kb}(K^2+K_o^2)\sin K_o a = 0 \quad . \tag{38}$$

This equation must be satisfied by all of the allowed values of B.

If B is real, then $P_I(x) \equiv 0$, and according to (33b), $P(x) = P_R(x)$ must be odd about the reflection symmetry points. For $P_1(x)$ to be odd about $x = -\frac{b}{2}$, we must have $B = \pm e^{-Kb}$. These real values of B, as easily seen from (37a), give $A\bar{A} = 1$, which in turn insures that $P_2(x)$ is real. $P_2(x)$ must also be odd about $x = \frac{a}{2}$. When inserted into equation (37) these values of B give

$$[2(K^2-K_o^2) S\bar{C} + 4K_o KC\bar{S}] = \pm 2(K^2+K_o^2) S \quad , \tag{39}$$

where S, C, $\bar{S}$, $\bar{C}$, are respectively $\sin K_o a$, $\cos K_o a$, $\sinh Kb$ and $\cosh Kb$.

If we assume that B takes on complex values then from equation (38) we have:

$$BB^* = e^{-2Kb} \; ; \quad B = e^{-Kb}e^{i\phi} \; , \; \phi \neq n\pi \quad .$$

This is exactly the condition which makes $P_I(x)$ even about $x = -\frac{b}{2}$, and $x = +\frac{a}{2}$. [It follows from $P_I(x)$ even that $P_R(x)$ is odd (equation 32a).] For B to be complex it is necessary that the discriminant of equation (38) be less than zero. This leads immediately to the result:

$$[2(K^2-K_o^2) S\bar{C} + 4K_o KC\bar{S}]^2 < 4(K^2+K_o^2)^2 S^2 \quad . \tag{40}$$

Hence the conditions (32c), (32d), (33a) and (33b) give rise to allowed energy levels when (39) and (40) are valid. That is, when

$$[2(K^2-K_0^2) s\bar{c} + 4K_0 K c\bar{s}]^2 \leqslant 4(K^2+K_0^2)^2 s^2 . \tag{41a}$$

The boundaries of the allowed regions correspond to real $P(x)$. The eigenfunctions at the tops and bottoms of the bands can be taken to be real. Also from $B = \pm e^{-Kb}$ we find that the boundary eigenfunctions are either purely symmetric or purely anti-symmetric. In fact the value $B = - e^{-Kb}$ gives the solution which is symmetric about $x = - \frac{b}{2}$ and corresponds to

$$(K^2-K_0^2) s\bar{c} + 2K_0 K c\bar{s} = + (K^2+K_0^2) s . \tag{41b}$$

$B = + e^{-Kb}$ gives the solution antisymmetric about $x = - \frac{b}{2}$ and corresponds to

$$(K^2-K_0^2) s\bar{c} + 2K_0 K c\bar{s} = - (K^2+K_0^2) s . \tag{41c}$$

Equation (41a) can be reduced fairly easily to the more familiar expression as follows:

$$[(K^2-K_0^2)s\bar{c} + 2K_0 K c\bar{s}]^2 - (K^2+K_0^2)^2 s^2 \leqslant 0 ,$$

$$(K^2-K_0^2)^2 s^2 \bar{c}^2 + 4K_0 K(K^2-K_0^2)sc\bar{s}\bar{c} + 4K_0^2 K^2 c^2 \bar{s}^2$$
$$- (K^2+K_0^2)^2 s^2 \leqslant 0 ,$$

$$(K^2-K_0^2)^2 s^2(1+\bar{s}^2) + 4K_0 K(K^2-K_0^2)sc\bar{s}\bar{c} + 4K_0^2 K^2(\bar{c}^2-1)c^2$$
$$-(K^2+K_0^2)^2 s^2 \leqslant 0 ,$$

$$(K^2-K_0^2)^2 s^2 \bar{s}^2 + 4K_0 K(K^2-K_0^2)sc\bar{s}\bar{c} + 4K_0^2 K^2 \bar{c}^2 c^2$$
$$+ (K^2-K_0^2)^2 s^2 - (K^2+K_0^2)^2 s^2 - 4K_0^2 K^2 c^2 \leqslant 0 ,$$

$$[(K^2-K_0^2)s\bar{s} + 2K_0 K c\bar{c}]^2 - 4K_0^2 K^2 \leqslant 0 ,$$

$$\left| \frac{(K^2-K_0^2)s\bar{s}}{2K_0 K} + c\bar{c} \right| \leqslant 1 . \tag{42}$$

We note here that although we have assumed the odd symmetry condition (33b) on $P_R(x)$ to discuss the case when B is real in order to effect a great deal of simplification, it is not necessary to do this. Instead we could use the fact that

$$\int_{\text{period}} P_R(x) \, dx = 0$$

to obtain another relation on B which together with (38) leads to the same results.

8. The Parabolic-Scallop Potential

In this example, we assume the periodic potential to be made up of a chain of segments of vertical parabolas opening upwards, Figure 4.

$$V(x) = \frac{1}{2} Kx^2 \; ; \; \frac{\ell}{2} \leqslant x \leqslant \frac{\ell}{2}$$

$$V(y) = y^2 \; ; \; -y_o \leqslant y \leqslant y_o$$
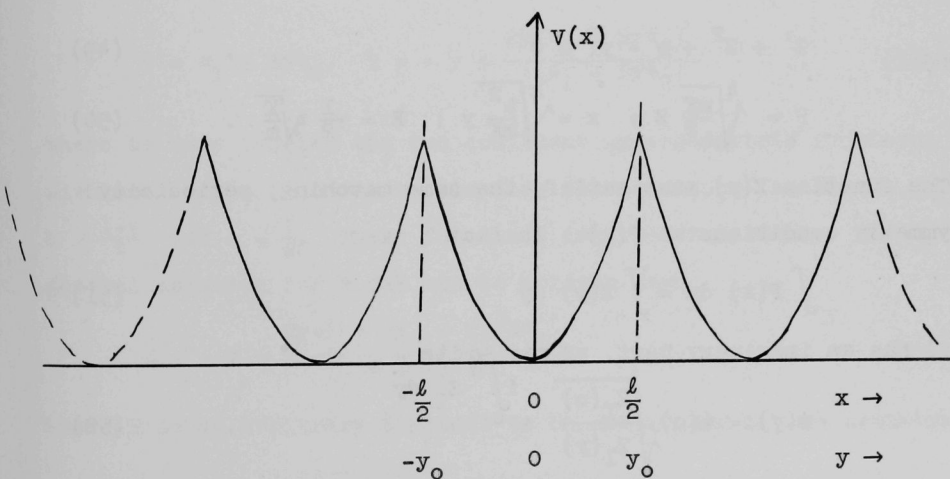
$$V(x + \ell) = V(x) \; ; \; V(y + 2y_o) = V(y)$$

Figure 4. Parabolic-Scallop Potential

The equation to be solved under the conditions of Section 6 is as follows:

$$P' + P^2 + \frac{2m}{\hbar^2}(E - \frac{1}{2}Kx^2) = 0 \tag{43}$$

Let

$$P = \alpha Z \; ; \; x = \beta y \tag{44}$$

Then,

$$\frac{\alpha}{\beta}\frac{dZ}{dy} + \alpha^2 Z^2 + \frac{2mE}{\hbar^2} - \frac{mK}{\hbar^2}\beta^2 y^2 = 0 \tag{45}$$

$$Z' + \beta\alpha Z^2 + \frac{2mE}{\hbar^2}\frac{\beta}{\alpha} - \frac{mK}{\hbar^2}\frac{\beta^3}{\alpha}y^2 = 0 \tag{46}$$

Let

$$\beta\alpha = 1 \; ; \; \frac{mK}{\hbar^2}\frac{\beta^3}{\alpha} = 1 \; , \; \frac{2mE}{\hbar^2}\frac{\beta}{\alpha} = \gamma \tag{47}$$

Then

$$\beta^4 = \frac{\hbar^2}{mK} \; ; \; \frac{\beta}{\alpha} = \beta^2 = \sqrt{\frac{\hbar^2}{mK}} \tag{48}$$

and

$$Z' + Z^2 + \gamma - y^2 = 0 \tag{49}$$

$$P = \sqrt[4]{\frac{mK}{\hbar^2}} Z \; ; \; x = \sqrt[4]{\frac{\hbar^2}{mK}} y \; ; \; E = \gamma\frac{1}{2}\hbar\sqrt{\frac{K}{m}} \tag{50}$$

The function $Z(y)$ must satisfy the same matching, periodicity and symmetry conditions as $P(x)$. In fact

$$\int P(x) \, dx = \int Z(y) \, dy \tag{51}$$

If $Z(y)$ has an imaginary part, we may write

$$\psi(y) = \psi(0)\sqrt{\frac{Z_I(0)}{Z_I(y)}} \; e^{i\int_0^y Z_I \, dy} \tag{52}$$

whereas for Z real we write

$$\psi(y) = \psi(0) \; e^{\int_0^y Z_R \, dy} \tag{53}$$

Equation (49) is a Ricatti equation. If we can find a particular solution, then we can get a general solution. A particular solution can easily be shown to be

$$Z_p = -y + \frac{2y\phi'}{\phi} \qquad , \qquad (53)$$

where $\phi = \phi(a,c; y^2) = \phi(\frac{1-\gamma}{4}, \frac{1}{2}; y^2)$ is the confluent hyper-geometric function as defined in Bateman.[4] This particular solution could be used to linearize the Ricatti equation and thus obtain the general solution by simple quadrature. However, it is simpler in the present case just to use for ϕ a general solution of the confluent hypergeometric differential equation. Such a solution suitable for our purposes (See Bateman, p. 253) is:

$$\phi \equiv \phi_1(a, c; y^2) + By^{2(1-c)}\phi_2(a-c+1, 2-c; y^2) \quad , \qquad (54a)$$

$$\phi = \phi_1 + By\phi_2, \quad Z = -y + \frac{2y(\phi_1 + By\phi_2)'}{(\phi_1 + By\phi_2)} \qquad , \qquad (54b)$$

where we have labeled the two confluent hypergeometric functions with subscripts in order to simplify the notation. As before, $a = \frac{1-\gamma}{4}$ and $c = \frac{1}{2}$. These functions are real functions. The general solution for Z can now be written down

$$Z = -y + \frac{2y\phi_1' + B\phi_2 + 2y^2 B\phi_2'}{\phi_1 + By\phi_2} \qquad , \qquad (55)$$

where B is an arbitrary constant to be determined by the symmetry

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[4]Bateman Manuscript Project, Higher Transcendental Functions V.1, Ch. VI, pp. 248-293, Erdelyi, Magnus, Oberhettinger and Tricomi, McGraw-Hill (1953).

conditions on Z, and the indicated derivatives are taken with respect to the variable y^2.

The periodicity relation (32c) now becomes

$$Z(-y_o) = Z(+y_o) \qquad , \qquad (56)$$

where $\beta y_o = \frac{\ell}{2}$. With a little algebra we find that

$$B^2(y_o, \gamma) = \left[\frac{\phi_1 (2\phi_1' - \phi_1)}{\phi_2 [\phi_2(1-y^2) + 2y^2\phi_2']} \right]_{y_o} \qquad (57)$$

from which we conclude that B is real or pure imaginary.

For B real, Z is real and we have from the symmetry condition (33b)

$$Z_R(-y) = - Z_R(-y) \qquad , \qquad (58)$$

which restricts B to the value zero. Since (54b) is so easy to integrate, it is actually simpler to use for real $Z(y)$ the condition (33c)

$$\int_{period} Z \, dy = 0 \qquad ,$$

instead of (58). Thus

$$\int Z \, dy = - \frac{y^2}{2} + \ln(\phi_1 + B y \phi_2) \qquad ,$$

$$\ln \frac{\phi_1(y_o) + By_o\phi_2(y_o)}{\phi_1(-y_o) - By_o\phi_2(-y_o)} = 0 \qquad ,$$

$$\frac{\phi_1(y_o) + By_o\phi_2(y_o)}{\phi_1(y_o) - By_o\phi_2(y_o)} = \pm 1 \qquad ,$$

from which it follows that either

$$\phi_1(y_o) = 0, \quad \phi_2(y_o) = 0, \quad B = 0, \quad \text{or} \quad B = \pm \infty \quad .$$

We see from (57) that $\phi_1(y_o) = 0$ requires $B = 0$ and $\phi_2(y_o) = 0$ gives $B = \pm \infty$ (or $\pm i\infty$ if B is not real). Since none of the properties are changed at infinite B whether $B = \pm \infty$ or $\pm i\infty$, we will ignore the possibility of $B = \pm \infty$ and include this infinite situation in the imaginary set. Hence the only real value of B which is allowed is $B = 0$.

When B is pure imaginary we must have from (57) that

$$\left[\frac{\phi_1}{\phi_2} \frac{(2\phi_1' - \phi_1)}{[\phi_2(1-y^2) + 2y^2\phi_2']} \right]_{y_o} < 0 \qquad . \qquad (59)$$

The condition (59) also insures that $Z_I(y)$ be even. The relation (59) supplemented by the condition $B = 0$ gives

$$B^2 = \left[\frac{\phi_1}{\phi_2} \frac{(2\phi_1' - \phi_1)}{\phi_2[\phi_2(1-y^2) + 2y^2\phi_2']} \right]_{y_o} \leqslant 0 \qquad , \qquad (60)$$

as the complete condition for the evaluation of the allowed bands as a function of the "lattice" parameter $2y_o$.

The eigenfunctions are easily calculated from the general expression

$$\psi(y) = \psi(o) \, e^{\int_o^y Z \, dy} \qquad . \qquad (61)$$

The value $B = 0$ gives the edges of those bands whose levels coalesce for infinite period y_o to the discrete levels of the isolated simple harmonic oscillator having eigenfunctions of even symmetry. In these cases

$$\psi(y) = \psi(o)\, e^{-y^2/2}\, \phi_1(\tfrac{1-\gamma}{4}, \tfrac{1}{2}; y^2) \qquad , \qquad (62)$$

where $\gamma = 4n + 1$ gives the discrete levels into which these bands coalesce. On the other hand $B = \pm i\infty$ gives the edges of the bands which arise from the antisymmetric simple harmonic oscillator levels; hence from equation (55), setting $B = \pm i\infty$,

$$Z = -y + \frac{\phi_2 + 2y^2\phi_2'}{y\phi_2} \qquad , \qquad (63a)$$

$$Z = -y + \frac{1}{y} + 2y\, \frac{d\ln\phi_2}{dy^2} \qquad , \qquad (63b)$$

$$\psi(y) = A\, e^{-y^2/2}\, y\phi_2(\tfrac{3-\gamma}{4}, \tfrac{3}{2}; y^2) \qquad , \qquad (63c)$$

where $\gamma = 4n + 3$ gives the limiting level of these bands.

A portion of the band structure obtained by considering the zeros of the numerator and denominator of the terms in expression (60) is given in Figure 5. Unfortunately tables of the confluent hypergeometric functions[5] are not sufficiently extensive and detailed to get a precise picture without further computation. The main features are, however, well illustrated. Note particularly that some forbidden regions exist for energies above the cusps of intersection of the parabolic segments. One notes also that as $y_0 \to 0$, edges of bands having opposite symmetry properties approach each other but touch and coalesce only in the limit of $y_0 = 0$. Thus the exceptional case discussed earlier arises only in the limit.

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[5] We have used "Confluent Hypergeometric Functions," L. S. Slater, Cambridge University Press, 1960 and "Tables of Functions," E. Jahnke and F. Emde, Dover Publications, 1943.

Fig. 5. Band Structure of Parabolic-Scallop Potential.

$V(x) = \frac{1}{2} kx^2$

$V(y) = y^2$

$\gamma = E / \frac{1}{2} \hbar \omega$

$[\phi_2 (1-y^2) + 2y^2 \phi_2']_{y_o} = [\ ]$
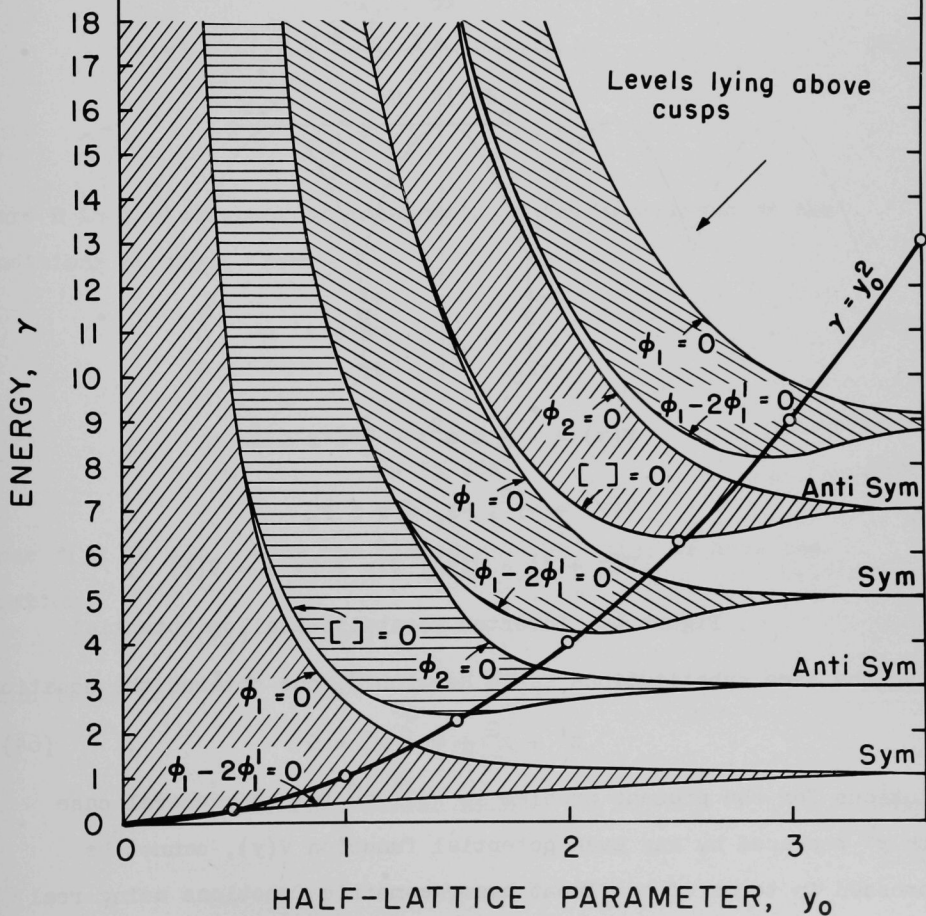
9. General Case One-Dimensional Infinitely Periodic and Even Potential

In this section the band structure problem for the general one-dimensional infinitely periodic even potential is considered. The general case is illustrated at various stages by reference to the potential shown in Figure 6, a chain of parabolic segments opening downwards.

$$V(x) = -\frac{1}{2} k x^2; \quad -\frac{\ell}{2} \leqslant x \leqslant \frac{\ell}{2} \qquad ,$$

$$V(y) = -y^2; \quad -y_o \leqslant y \leqslant y_o \qquad ,$$
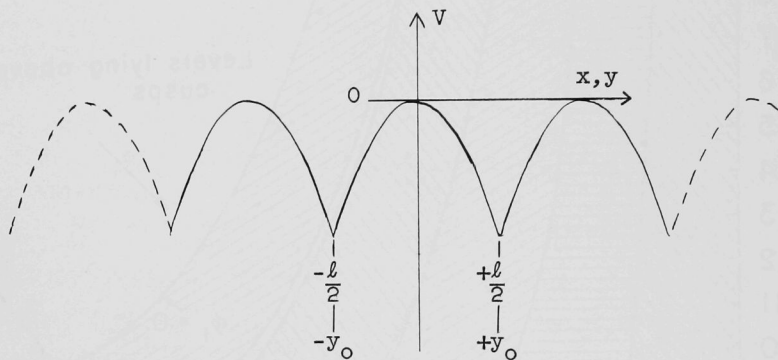
$$V(x + \ell) = V(x); \quad V(y + 2y_o) = V(y) \quad .$$

Figure 6. Inverted Parabolic-Scallop Potential

Using the same substitutions as in Section 8, one obtains the equation

$$z' + z^2 + \gamma + y^2 = 0 \qquad . \qquad (64)$$

Solutions for the present problem as well as for the general case with y^2 replaced by any even potential function $V(y)$, cannot be expressed in terms of confluent hypergeometric functions using real parameters and real variables. Bessel functions or other tabulated functions will also not suffice. Another approach must be taken.

Clearly a particular solution of (64) can be obtained (in series form or otherwise) which is purely odd for then all terms in (64) will be even. Let such a solution be $f(\gamma,y)$. With this $f(y)$ -- for simplicity we drop from time to time the explicit indication of the dependency on the energy γ -- the complete solution of (64) becomes

$$z(y) = f(y) + \frac{e^{-2\int_0^y f\,du}}{\int_0^y e^{-2\int_0^u f(v)dv}\,du + B} \quad , \tag{65}$$

where B is the constant of integration to be determined by the conditions on $z(y)$. Now

$$\int_0^y f\,du \text{ is even} \quad , \tag{66a}$$

$$\int_0^y e^{-2\int_0^u f(v)dv}\,du \text{ is odd} \quad , \tag{66b}$$

since $f(y)$ is odd. From the periodicity relation we have the equation

$$z(y_0) = z(-y_0) \quad , \tag{67}$$

which leads to

$$B^2 = \frac{I_0[I_0 f_0 + e^{-2\int_0^{y_0} f(u)du}]}{f_0} \quad , \tag{68a}$$

where

$$I_o(y_o) \equiv I_o = \int_0^u e^{y_o -2\int_0^u f(v)dv} \, du \qquad , \qquad (68b)$$

$$f_o \equiv f(\gamma, y_o) \qquad . \qquad (68c)$$

We see from (68a) that B must be real or pure imaginary. If it is real then the odd symmetry of $z(y)$ or alternatively equation (33e) shows that $B = 0$. Hence we are left with the condition that

$$B^2 = \frac{I_o[I_o f_o + e^{-2\int_0^{y_o} f(u)du}]}{f_o} \leqslant 0 \qquad . \qquad (69)$$

When (69) is satisfied we will have the allowed band structure of the inverted parabolic potential. From (68b) we see that I_o is always positive ($y_o > 0$). Hence the allowed regions are given by

$$\frac{I_o f_o + e^{-2\int_0^{y_o} f(u)du}}{f_o} \leqslant 0 \qquad . \qquad (70)$$

Since $f(\gamma,y)$ is a particular solution of (64) with $f(\gamma,o) = 0$, it starts out with a slope $-\gamma$. Hence for negative energy states, $f_o \geqslant 0$ from $y_o = 0$ up to the first sign change $f_o(\gamma, y_o)$. A forbidden zone exists immediately below $\gamma = 0$ whose width is determined by the lattice parameter y_o.

Unfortunately the particular solution $f(\gamma, y_o)$ will not be well-behaved in general; it will have infinite discontinuities. We can see this by realizing that the most general "particular solution" we can have for the real function f is

$$f = \frac{\phi_S' + B_1 \phi_A'}{\phi_S + B_1 \phi_A} \qquad , \qquad (71)$$

where B_1 is real and ϕ_S and ϕ_A are respectively the symmetric and antisymmetric eigensolutions of the Schroedinger equation:

$$\phi'' + (\gamma + y^2)\phi = 0 \qquad . \qquad (72)$$

In general there would not be a choice of B_1 which would insure that the denominator of (71) have no zeros. For example, suppose we choose

$$f = \frac{\phi_S'}{\phi_S} \qquad , \qquad (73)$$

where $\phi_S(\gamma,o) = 1$. Then (65) becomes

$$Z(y) = \frac{\phi_S'}{\phi_S} + \frac{e^{-2\int_0^y \frac{\phi_S'}{\phi_S} dy}}{\int_0^y e^{-2\int_0^u \frac{\phi_S'}{\phi_S} dv} du + B} \qquad , \qquad (74)$$

$$Z(y) = \frac{\phi_S'}{\phi_S} + \frac{1}{\phi_S^2 \left[\int_0^y \frac{1}{\phi_S^2} du + B \right]} \qquad , \qquad (75)$$

$$Z(y_o) = \left[\frac{1}{\phi_S}(\phi_S' + \frac{1}{\phi_S I + B\phi_S}) \right]_{y_o} \qquad . \qquad (76)$$

If for a certain γ, $y = y_1$ corresponds to the first zero of $\phi_S(\gamma,y)$, then the integral $I_o = \int_0^{y_o} \frac{du}{\phi_S^2}$ in the above equations becomes infinite

at $y_o = y_1$. Hence the analysis described in equations (65-69) would not be applicable for $y_o > y_1$! This poses a dilemma.

Although the integral $I(y_o)$ becomes infinite at $y_o = y_1$, one can easily show that $\phi_S I$ does not become infinite. Hence, if $\phi_S I$ can be replaced by some new calculable function which is identical with $\phi_S I$ for $y_o < y_1$ and which carries over into the region beyond $y_o = y_1$ without becoming infinite, then our dilemma will be removed. Let us examine the properties of $\phi_S I$.

$$\psi = \phi_S I = \phi_S \int_o^y \frac{du}{\phi_S^2} \qquad , \qquad (77a)$$

$$\psi' = \phi_S' I + \frac{1}{\phi_S} \qquad , \qquad (77b)$$

$$\psi'' = \phi_S'' I + \frac{\phi_S'}{\phi_S^2} - \frac{\phi_S'}{\phi_S^2} = \phi_S'' \frac{\psi}{\phi_S} \qquad , \qquad (77c)$$

$$\psi'' = - (\gamma + y^2)\psi \qquad . \qquad (77d)$$

Hence $\psi(y)$ obeys the same Schroedinger equation as does ϕ_S. Furthermore $\psi(o) = 0$ and $\psi'(o) = 1$; hence ψ is just the anti-symmetrical solution ϕ_A;

$$\phi_A = \phi_S I \qquad . \qquad (78)$$

Equation (75) can now be written

$$z(y) = \frac{1}{\phi_S} [\phi_S' + \frac{1}{\phi_A + B\phi_S}] \qquad . \qquad (79)$$

Equation (79) is a perfectly general solution of equation (64), or for that matter of any periodic one-dimensional even potential problem where ϕ_S and ϕ_A are the correspondingly appropriate symmetrical and antisymmetrical solutions. With these solutions, equation (69) reduces to

$$B^2 = \left.\frac{\phi_A \phi_A'}{\phi_S \phi_S'}\right|_{y_0} \leqslant 0 \qquad , \qquad (80)$$

as the general expression for the determination of the band structure. The band edges correspond to $B = 0$ or $\pm i\infty$ and lead as before to Bloch k values of 0 and $\pi/2y_0$. The eigenfunctions at the band edges are:

$$\left.\begin{cases} \psi_A(y) = \phi_A; \quad (B = 0) \\ [k = 0 \text{ for } \phi_A(y_0) = 0; \quad k = \frac{\pi}{2y_0} \text{ for } \phi_A'(y_0) = 0] \end{cases}\right\}, \qquad (81a)$$

$$\left.\begin{cases} \psi_S(y) = \phi_S; \quad (B = \pm i\infty) \\ [k = 0 \text{ for } \phi_S'(y_0) = 0; \quad k = \frac{\pi}{2y_0} \text{ for } \phi_S(y_0) = 0] \end{cases}\right\}. \qquad (81b)$$

Inside the bands we have $B = iC$, $C \neq 0$ or ∞,

$$C^2 = \left. -\frac{\phi_A \phi_A'}{\phi_S \phi_S'}\right|_{y_0} \qquad , \qquad (82a)$$

$$z(y) = \frac{1}{\phi_S}\left[\phi_S' + \frac{1}{\phi_A + iC\phi_S}\right] \qquad , \qquad (82b)$$

$$\psi(y) = \phi_A + iC\phi_S \qquad . \qquad (82c)$$

The last equation is the result of integration of (82b) using the fact that the Wronskian is a constant and equal to one; $\phi_S \phi_A' - \phi_S' \phi_A = 1$. Also we have from (82b) the relation

$$z_I(y) = \frac{-C}{\phi_A^2 + C^2\phi_S^2} \qquad , \qquad (83)$$

from which it follows that the Bloch k value is given by

$$k = -\frac{C}{y_o} \int_o^{y_o} \frac{dy}{\phi_A{}^2 + C^2\phi_S{}^2} \qquad , \qquad (84a)$$

$$ky_o = \tan^{-1} \frac{C\phi_S}{\phi_A} - \frac{\pi}{2} \qquad , \qquad (84b)$$

$$\tan ky_o = -\frac{\phi_A}{C\phi_S} \qquad , \qquad (84c)$$

$$\sin^2 ky_o = -\phi_A(y_o)\, \phi_S'(y_o) \qquad . \qquad (84d)$$

Actually equations (80-84) could have been derived very simply from the periodicity relation on $|\psi|^2$ and the matching condition on the logarithmic derivative at the cell wall. (See Appendix III). Thus we have gone in a full circle. However, by this route we have learned how to calculate the eigenfunctions within the allowed bands and the relations between our treatment and the Bloch method.

The completion of the band structure calculation for our specific example - the inverted parabolic-scallop potential - is a simple machine computational exercise. The infinite series solutions of (72) for $\phi_S(\gamma,y)$ and $\phi_A(\gamma,y)$ are used to calculate the two functions and their first derivatives for various values of γ and y. For a given value of the half lattice parameter, $y = y_o$, one seeks those values of γ which make the functions or their first derivatives zero. Alternatively, for a given γ, one seeks the values of the half-lattice parameter, $y = y_o$, which makes the functions and derivatives vanish.

TABLE I. LOCI OF POINTS OF γ VS y_o-INVERTED PARABOLIC SCALLOP POTENTIAL

γ	y_o			
	$\phi_S(y_o) = 0$	$\phi_S'(y_o) = 0$	$\phi_A(y_o) = 0$	$\phi_A'(y_o) = 0$
2.0	1.0709 2.4477 3.4107 4.1849 4.8482	1.8072 2.9482 3.8081 4.5231	1.8204 2.9477 3.8044 4.5185	0.9882 2.4131 3.3898 4.1696 4.8359
1.9	1.0948 2.4731 3.4341 4.2066 4.8686	1.8327 2.9726 3.8306 4.5442	1.8432 2.9699 3.8251 4.5380	1.0047 2.4358 3.4112 4.1897 4.8549
1.8	1.1202 2.4992 3.4581 4.2288 4.8894	1.8592 2.9976 3.8536 4.5656	1.8664 2.9924 3.8460 4.5576	1.0218 2.4589 3.4329 4.2099 4.8741
1.7	1.1472 2.5263 3.4827 4.2515 4.9106	1.8870 3.0234 3.8773 4.5876	1.8902 3.0151 3.8672 4.5775	1.0395 2.4823 3.4549 4.2305 4.8933
1.6	1.1761 2.5542 3.5079 4.2748 4.9323	1.9160 3.0500 3.9015 4.6100	1.9145 3.0382 3.8886 4.5975	1.0579 2.5061 3.4771 4.2511 4.9128
1.5	1.2068 2.5832 3.5340 4.2986 4.9546	1.9464 3.0774 3.9264 4.6331	1.9393 3.0615 3.9102 4.6177	1.0771 2.5303 3.4995 4.2720 4.9324
1.4	1.2398 2.6133 3.5608 4.3232 4.9774	1.9783 3.1058 3.9520 4.6567	1.9646 3.0851 3.9320 4.6381	1.0969 2.5549 3.5222 4.2931 4.9521
1.3	1.2750 2.6446 3.5886 4.3485 5.0009	2.0119 3.1352 3.9785 4.6811	1.9903 3.1090 3.9540 4.6586	1.1175 2.5798 3.5451 4.3143 4.9721

TABLE I (Continued)

γ	y_o			
	$\phi_S(y_o) = 0$	$\phi_S'(y_o) = 0$	$\phi_A(y_o) = 0$	$\phi_A'(y_o) = 0$
1.2	1.3129 2.6772 3.6173 4.3746 5.0252	2.0472 3.1658 4.0058 4.7062	2.0165 3.1331 3.9762 4.6793	1.1387 2.6050 3.5682 4.3357 4.9921
1.1	1.3535 2.7113 3.6471 4.4016 5.0502	2.0845 3.1976 4.0342 4.7322	2.0432 3.1575 3.9985 4.7001	1.1610 2.6306 3.5915 4.3573 5.0123
1.0	1.3970 2.7470 3.6781 4.4296 5.0761	2.1239 3.2307 4.0636 4.7591	2.0703 3.1821 4.0211 4.7211	1.1839 2.6565 3.6150 4.3790 5.0327
0.9	1.4438 2.7844 3.7105 4.4588	2.1656 3.2654 4.0943 4.7870	2.0978 3.2070 4.0438 4.7422	1.2076 2.6826 3.6388 4.4008 5.0531
0.8	1.4939 2.8236 3.7442 4.4891	2.2096 3.3016 4.1262 4.8161	2.1256 3.2320 4.0666 4.7634	1.2321 2.7090 3.6626 4.4228 5.0737
0.7	1.5476 2.8648 3.7794 4.5206	2.2562 3.3396 4.1594 4.8463	2.1539 3.2572 4.0896 4.7847	1.2574 2.7357 3.6867 4.4450 5.0944
0.6	1.6047 2.9079 3.8162 4.5535	2.3053 3.3793 4.1942 4.8778	2.1825 3.2825 4.1126 4.8061	1.2835 2.7627 3.7108 4.4672
0.5	1.6652 2.9531 3.8545 4.5877	2.3570 3.4207 4.2303 4.9105	2.2112 3.3081 4.1358 4.8277	1.3104 2.7897 3.7351 4.4895

TABLE I (Continued)

γ	y_o			
	$\phi_S(y_o) = 0$	$\phi_S'(y_o) = 0$	$\phi_A(y_o) = 0$	$\phi_A'(y_o) = 0$
0.4	1.7290	2.4110	2.2403	1.3380
	3.0001	3.4638	3.3337	2.8170
	3.8943	4.2678	4.1591	3.7595
	4.6232	4.9444	4.8492	4.5119
0.3	1.7954	2.4671	2.2696	1.3663
	3.0488	3.5084	3.3594	2.8444
	3.9355	4.3066	4.1824	3.7840
	4.6599	4.9794	4.8708	4.5343
0.2	1.8638	2.5248	2.2990	1.3952
	3.0989	3.5542	3.3852	2.8719
	3.9777	4.3464	4.2058	3.8085
	4.6975	5.0153	4.8925	4.5568
0.1	1.9334	2.5835	2.3286	1.4248
	3.1498	3.6008	3.4110	2.8995
	4.0207	4.3868	4.2292	3.8330
	4.7357	5.0518	4.9142	4.5793
0.0	2.0031	2.6423	2.3599	1.4538
	3.2010	3.6476	3.4364	2.9245
	4.0640	4.4275	4.2535	3.8551
	4.7741	5.0898	4.9333	4.6007
-0.1	2.0721	0.5471	2.3880	1.4857
	3.2518	2.7007	3.4620	2.9549
	4.1070	3.6942	4.2761	3.8820
	4.8125	4.4681	4.9575	4.6242
-0.2	2.1393	0.7711	2.4178	1.5168
	3.3016	2.7578	3.4886	2.9824
	4.1494	3.7400	4.2994	3.9066
	4.8503	4.5080	4.9791	4.6467
-0.3	2.2039	0.9394	2.4476	1.5483
	3.3501	2.8131	3.5143	3.0100
	4.1906	3.7845	4.3227	3.9311
	4.8872	4.5470	5.0007	4.6691
-0.4	2.2656	1.0770	2.4773	1.5802
	3.3967	2.8660	3.5400	3.0375
	4.2305	3.8274	4.3459	3.9555
	4.9229	4.5846	5.0222	4.6914

TABLE I (Continued)

| γ	y_o			
	$\phi_S(y_o) = 0$	$\phi_S'(y_o) = 0$	$\phi_A(y_o) = 0$	$\phi_A'(y_o) = 0$
-0.5	2.3240 3.4412 4.2687 4.9573	1.1939 2.9164 3.8686 4.6208	2.5069 3.5656 4.3690 5.0436	1.6122 3.0649 3.9797 4.7137
-0.6	2.3791 3.4836 4.3053 4.9902	1.2954 2.9642 3.9078 4.6555	2.5363 3.5910 4.3920 5.0650	1.6445 3.0922 4.0039 4.7359
-0.7	2.4308 3.5239 4.3402 5.0217	1.3847 3.0094 3.9452 4.6886	2.5657 3.6163 4.4149 5.0862	1.6769 3.1193 4.0279 4.7578
-0.8	2.4795 3.5622 4.3735 5.0519	1.4643 3.0521 3.9808 4.7202	2.5948 3.6415 4.4377	1.7093 3.1463 4.0518 4.7797
-0.9	2.5253 3.5986 4.4053 5.0807	1.5359 3.0925 4.0147 4.7504	2.6238 3.6664 4.4603	1.7417 3.1731 4.0755 4.8015
-1.0	2.5685 3.6332 4.4356	1.6010 3.1308 4.0470 4.7794	2.6525 3.6912 4.4828	1.7740 3.1996 4.0991 4.8231
-1.1	2.6094 3.6662 4.4648	1.6605 3.1673 4.0779 4.8071	2.6809 3.7158 4.5050	1.8063 3.2260 4.1224 4.8445
-1.2	2.6482 3.6979 4.4927	1.7154 3.2020 4.1076 4.8339	2.7091 3.7402 4.5271	1.8383 3.2521 4.1456 4.8658
-1.3	2.6852 3.7282 4.5197	1.7665 3.2353 4.1361 4.8596	2.7371 3.7643 4.5490	1.8702 3.2779 4.1685 4.8869

TABLE I (Continued)

| γ	y_0			
	$\phi_S(y_0) = 0$	$\phi'_S(y_0) = 0$	$\phi_A(y_0) = 0$	$\phi'_A(y_0) = 0$
-1.4	2.7206 3.7575 4.5457	1.8142 3.2672 4.1636 4.8845	2.7647 3.7882 4.5708	1.9018 3.3035 4.1913 4.9078
-1.5	2.7545 3.7857 4.5709	1.8591 3.2979 4.1902 4.9087	2.7920 3.8119 4.5923	1.9331 3.3288 4.2138 4.9285
-1.6	2.7871 3.8130 4.5954	1.9015 3.3275 4.2160 4.9321	2.8190 3.8353 4.6136	1.9641 3.3539 4.2361 4.9491
-1.7	2.8186 3.8395 4.6192	1.9418 3.3562 4.2411 4.9550	2.8458 3.8585 4.6347	1.9948 3.3787 4.2582 4.9694
-1.8	2.8490 3.8653 4.6424	1.9803 3.3841 4.2655 4.9773	2.8721 3.8815 4.6556	2.0252 3.4301 4.2801 4.9896
-1.9	2.8786 3.8904 4.6650	2.0172 3.4112 4.2893 4.9990	2.8983 3.9042 4.6763	2.0552 3.4274 4.3018 5.0096

The functions $\phi_S(\gamma,y)$, $\phi_A(\gamma,y)$, $\phi'_S(\gamma,y)$ and $\phi'_A(\gamma,y)$ are available at Argonne National Laboratory for the ranges $-2.0 \leqslant \gamma \leqslant +2.0$, $-5 \leqslant y \leqslant +5$ for intervals $\Delta y = 0.1$ and $\Delta\gamma = 0.1$. These tables of functions make it possible to calculate $C(\gamma,y_0)$ from equation (82a), the eigenfunctions $\psi(\gamma,y_0; y)$ from equation (82c), and the Bloch k value from equation (84d) for any situation within the allowed energy regions.

Table I gives the values of the energy γ and the corresponding values of y_0 for which the two functions and their first derivatives vanish. The curves of γ vs y_0 for each of these functions is plotted in Figure 7. The allowed regions for which $c^2 > 0$ is cross-hatched. The curve marked $\gamma = y_0^2$ gives the bottom of the potential well which occurs in our choice of coordinates at $y = \pm y_0$, $\pm 3y_0$, $\pm 5y_0$,... It·is clear from the figure that until a certain depth is reached there can be only one band below $E = 0$. Also, for a given y_0 not too large there is an allowed band that spans both positive and negative energies about $\gamma = 0$ ($E = 0$). Contrary to the case of the potential consisting of parabolic segments opening upwards, each discrete level at infinite separation belongs to eigenfunctions of both symmetry class. For example, the lowest band has boundaries which correspond to $\phi_S'(y_0) = 0$ and $\phi_A'(y_0) = 0$ and appears to arise from a symmetrical function about $y = 0$ which goes to zero in the middle of the infinitely deep well and an antisymmetrical function which also goes to zero in the middle of the infinitely deep well. Both are pushed up by the juxtaposition of other potentials but they retain their zero slopes at $\pm y_0$. If one considers the symmetries of the functions about the center of the well -- as was the case for the parabolas opening upwards -- then the top and bottom of each allowed band has eigenfunctions of the same symmetry. Finally one notices that the tops of the bands and hence the discrete levels at infinite y_0 assume a.linear relation in y_0 as γ becomes more and more negative. Thus, the energies of the bands measured from the bottom of the well get larger quadratically as y_0 increases.

Fig. 7. Band Structure—Inverted Parabolic Scallop Potential.
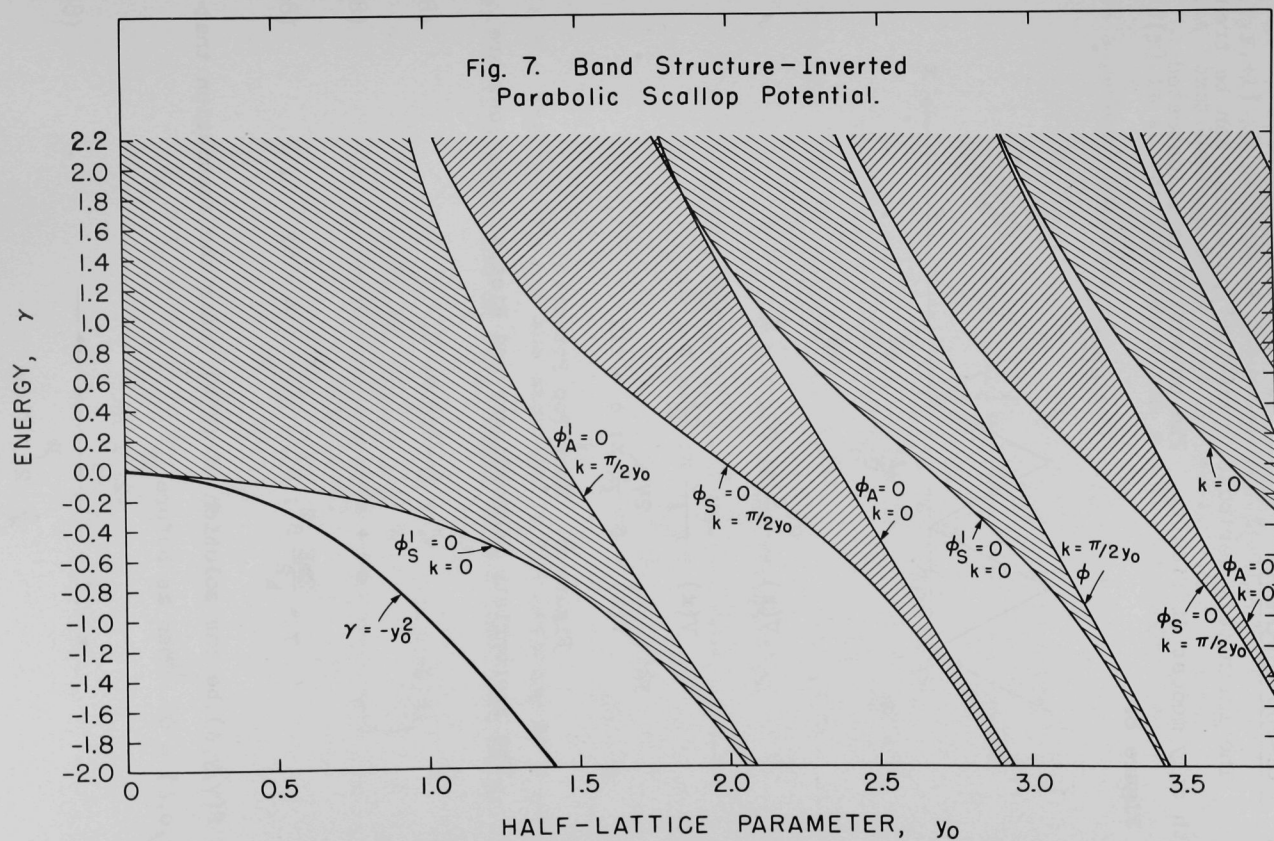
10. Roof-Top Potential

The infinitely periodic "roof-top" potential can be treated with only modest difficulty. The potential is illustrated in Figure 8.

$$V(x) = \frac{2V_o}{\ell} x; \quad 0 \leqslant x \leqslant \frac{\ell}{2}$$

$$V(x) = \frac{-2V_o}{\ell} x; \quad \frac{-\ell}{2} \leqslant x \leqslant 0,$$
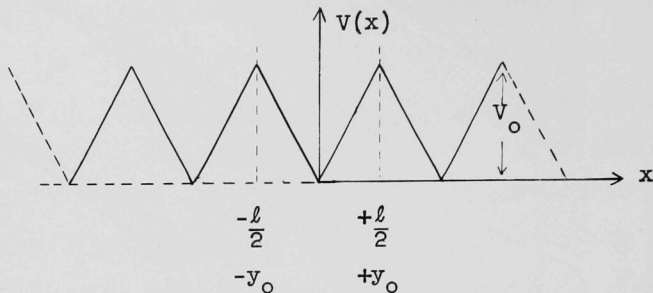
$$V(x) = \delta \frac{2V_o}{\ell} x; \quad \delta = \pm 1.$$

Figure 8. Roof-Top Potential

The appropriate Schroedinger and Ricatti equations are:

$$\phi'' + (\gamma - \delta y)\, \phi = 0, \tag{85a}$$

$$z' + z^2 + \gamma - \delta y = 0, \tag{85b}$$

$$\gamma = \frac{2mE}{\hbar^2}\beta^2; \quad \beta^3 = \frac{\ell\hbar^2}{4mV_o}; \quad x = \beta y \quad . \tag{85c}$$

Let $f(\gamma, y, \delta)$ be the solution of (85b) under the assumption that $f(\gamma, o, \delta) = 0$. Then as before

$$z = f + \frac{e^{-2\int_o^y f\, du}}{\int_o^y e^{-2\int_o^u f\, dv}\, du + B} \quad . \tag{86}$$

Now $f(\gamma,y,+1)$ is to be used for $y > 0$ and $f(\gamma,y,-1)$ for $y < 0$. A little consideration shows that $f(\gamma,y,+1) = -f(\gamma,-y,-1)$. Hence $f(y)$ is an odd function about $y = 0$. As in Section 9, we have a general solution

$$z(y) = f(\gamma,y,+1) + \frac{e^{-2\int_0^y f(\gamma,u,+1)\,du}}{\int_0^y e^{-2\int_0^u f(\gamma,v,+1)\,dv}\,du + B} \tag{87}$$

for $y > 0$ and

$$z(y) = f(\gamma,y,-1) + \frac{e^{-2\int_0^y f(\gamma,u,-1)\,du}}{\int_0^y e^{-2\int_0^u f(\gamma,v,-1)\,dv}\,du + B} \tag{88}$$

for $y \leqslant 0$. The two B's are the same due to the matching at $y = 0$. The periodicity condition on $z(y_0)$ leads to the condition on B:

$$B^2 = \frac{I_0\left\{I_0 f(\gamma,y_0,+1) + e^{-2\int_0^{y_0} f(\gamma,u,+1)\,du}\right\}}{f(\gamma,y_0,+1)} , \tag{89}$$

where

$$I_0 \equiv I_0(\gamma,y_0) = \int_0^{y_0} e^{-2\int_0^u f(\gamma,v,+1)\,dv}\,du . \tag{90}$$

Since I_o is always positive we are lead exactly as in Section 9 to the inequality which must be met to have allowed levels:

$$\frac{I_o f(\gamma,y_o,+1) + e^{-2\int_0^{y_o} f(\gamma,u,+1)du}}{f(\gamma,y_o,+1)} \leqslant 0 \quad . \quad (91)$$

In principle it is a very simple machine computational problem to calculate $f(\gamma,y_o,+1)$ from the equations

$$f' + f^2 + \gamma - y = 0 \quad , \quad (92a)$$

$$f(\gamma,o,+1) = 0 \quad , \quad (92b)$$

and, in turn to calculate the other terms in (91) for y_o values up to the first sign change of $f(\gamma,y_o,+1)$. Clearly f starts out at zero with a negative slope (for $\gamma > 0$); hence there is an allowed band for each γ starting from $y_o = 0$.

In order to continue the calculations beyond the first sign change of $f(\gamma,y_o,+1)$ it is necessary to proceed as illustrated in Section 9. We take $f(\gamma,y_o,+1)$ to be the logarithmic derivative of the symmetrical solution of the Schroedinger equation (85a):

$$f(\gamma,y,+1)e \equiv \frac{\phi_S'(\gamma,y,+1)}{\phi_S(\gamma,y,+1)} \quad . \quad (93)$$

Now $\phi_S(\gamma,y,\pm1)$ can be expressed in terms of Bessel functions. The results are:

$$\phi_S(\gamma,y,+1) = \sqrt{\gamma-y} \ [A_1 \ J_{\frac{1}{3}}\{\tfrac{2}{3}(\gamma-y)^{\frac{3}{2}}\} + B_1 \ J_{-\frac{1}{3}}\{\tfrac{2}{3}(\gamma-y)^{\frac{3}{2}}\}] \ , \quad (94a)$$

$$\phi_S(\gamma,-y,-1) = \sqrt{\gamma+y} \; [A_2 J_{\frac{1}{3}}\left\{\frac{2}{3}(\gamma+y)^{\frac{3}{2}}\right\} + B_2 \; J_{-\frac{1}{3}}\left\{\frac{2}{3}(\gamma+y)^{\frac{3}{2}}\right\}] \quad . \quad (94b)$$

It is easy to see that if we choose $A_2 = A_1$, $B_2 = B_1$, then

$$\phi_S(\gamma,-y,+1) = \phi_S(\gamma,y,-1) \qquad . \qquad (95)$$

Hence (94a, 94b) do indeed represent a symmetrical solution. The solution will be smooth across $y = 0$, that is the logarithmic derivative will match, if we choose A and B so that $\phi'(\gamma,0,\pm 1) = 0$. Similarly we can obtain an antisymmetrical solution if we set

$$\phi_A(\gamma,y,+1) = \sqrt{\gamma-y} \; [C_1 \; J_{\frac{1}{3}}\left\{\frac{2}{3}(\gamma-y)^{\frac{3}{2}}\right\} + D_1 \; J_{-\frac{1}{3}}\left\{\frac{2}{3}(\gamma-y)^{\frac{3}{2}}\right\}] \quad , \quad (96a)$$

$$\phi_A(\gamma,y,-1) = \sqrt{\gamma+y} \; [C_1 \; J_{\frac{1}{3}}\left\{\frac{2}{3}(\gamma+y)^{\frac{3}{2}}\right\} + D_1 \; J_{-\frac{1}{3}}\left\{\frac{2}{3}(\gamma+y)^{\frac{3}{2}}\right\}] \quad , \quad (96b)$$

where C_1 and D_1 are chosen in such a way to make $\phi_A(\gamma,0,\pm 1) = 0$. Thus we have the two conditions:

$$\frac{-1}{2\sqrt{\gamma}} \; [A_1 \; J_{\frac{1}{3}}(\frac{2\gamma^{\frac{3}{2}}}{3}) + B_1 \; J_{-\frac{1}{3}}(\frac{2\gamma^{\frac{3}{2}}}{3})] - \gamma[A_1 \; J'_{\frac{1}{3}}(\frac{2\gamma^{\frac{3}{2}}}{3}) + B_1 \; J'_{-\frac{1}{3}}(\frac{2\gamma^{\frac{3}{2}}}{3})] = 0, \quad (97a)$$

$$C_1 \; J_{\frac{1}{3}}(\frac{2\gamma^{\frac{3}{2}}}{3}) + D_1 \; J_{-\frac{1}{3}}(\frac{2\gamma^{\frac{3}{2}}}{3}) = 0 \qquad . \qquad (97b)$$

Equation (97a) may be reduced to the following relation after using appropriate recursion formulae connecting derivatives and functions:[6]

---

[6]"Bessel Functions for Engineers", N. W. McLachlan, Oxford University Press, 1941, p.24.

$$r(\gamma) = \frac{J_{\frac{2}{3}}(\frac{2\gamma^{\frac{3}{2}}}{3})}{J_{-\frac{2}{3}}(\frac{2\gamma^{\frac{3}{2}}}{3})} \quad ; \quad A_1 = rB_1 \qquad . \qquad (98a)$$

Similarly (97b) reduces to the relation

$$s(\gamma) = -\frac{J_{-\frac{1}{3}}(\frac{2\gamma^{\frac{3}{2}}}{3})}{J_{+\frac{1}{3}}(\frac{2\gamma^{\frac{3}{2}}}{3})} \quad ; \quad C_1 = sD_1 \qquad . \qquad (98b)$$

The edges of the allowed bands will be given by the zeros of $\phi_S(y_o)$, $\phi_S'(y_o)$, $\phi_A(y_o)$, and $\phi_A'(y_o)$ where we insert (98a) and (98b) into (94a) and (96a). For the energy region below the ridge of the roof, $\gamma < y_o$, the argument in the Bessel functions is imaginary and it is convenient to replace the ordinary Bessel functions $J_{\pm\frac{1}{3}}\left\{\frac{2}{3}(\gamma-y)^{\frac{2}{3}}\right\}$ by the modified Bessel functions $I_{\pm\frac{1}{3}}\left\{\frac{2}{3}(y-\gamma)^{\frac{2}{3}}\right\}$ in equations (94a) and (94b). With these substitutions we obtain the following equations. For

$$y_o > \gamma, \ x = \frac{2}{3}(y_o-\gamma)^{\frac{3}{2}} \qquad , \qquad (99a)$$

$$\phi_S(x) = Bx^{\frac{1}{3}}\left\{-rI_{\frac{1}{3}}(x) + I_{-\frac{1}{3}}(x)\right\} \qquad , \qquad (99b)$$

$$\frac{d\phi_S(x)}{dy}\bigg|_{y_o} = Bx^{\frac{2}{3}}\left\{-rI_{-\frac{2}{3}}(x) + I_{\frac{2}{3}}(x)\right\} \qquad , \qquad (99c)$$

$$\phi_A(x) = Dx^{\frac{1}{3}}\left\{-sI_{\frac{1}{3}}(x) + I_{-\frac{1}{3}}(x)\right\} \qquad , \qquad (99d)$$

$$\frac{d\phi_A(x)}{dy}\bigg|_{y_o} = Dx^{\frac{2}{3}}\left\{-sI_{-\frac{2}{3}}(x) + I_{\frac{2}{3}}(x)\right\} \qquad . \qquad (99e)$$

For

$$y_o < \gamma, \quad z = \frac{2}{3}(\gamma-y_o)^{\frac{3}{2}} \qquad , \qquad (100a)$$

$$\phi_S(z) = Bz^{\frac{1}{3}}\left\{rJ_{\frac{1}{3}}(z) + J_{-\frac{1}{3}}(z)\right\} \qquad , \qquad (100b)$$

$$\frac{d\phi_S(z)}{dy}\bigg|_{y_o} = -Bz^{\frac{2}{3}}\left\{rJ_{-\frac{2}{3}}(z) + J_{\frac{2}{3}}(z)\right\} \qquad , \qquad (100c)$$

$$\phi_A(z) = Dz^{\frac{1}{3}}\left\{sJ_{\frac{1}{3}}(z) + J_{-\frac{1}{3}}(z)\right\} \qquad , \qquad (100d)$$

$$\frac{d\phi_A(z)}{dy}\bigg|_{y_o} = -Dz^{\frac{2}{3}}\left\{sJ_{-\frac{2}{3}}(z) + J_{\frac{2}{3}}(z)\right\} \qquad . \qquad (100e)$$

It is easy to see that the above equations do indeed have the appropriate properties. For example (100c) and 100d) are zero for $y = 0$. Also equations (99) match equations (100) at $y_o = \gamma$. It is clear from equations (99) and the fact that $I_\nu(x)$ and $I_{-\nu}(x)$ approach each other at large x that the symmetric bands start from discrete levels given by $r(\gamma) = 1$ and the antisymmetric bands start from discrete levels given by $s(\gamma) = 1$. The entire band structure can be mapped out using the NBS Tables.[7] The results are illustrated in Figure 9.

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[7]"Tables of Bessel Functions of Fractional Order", Vol. 1 and 2, National Bureau of Standards, Columbia University Press, 1948.

Fig. 9. Band Structure
Roof Top Potential.
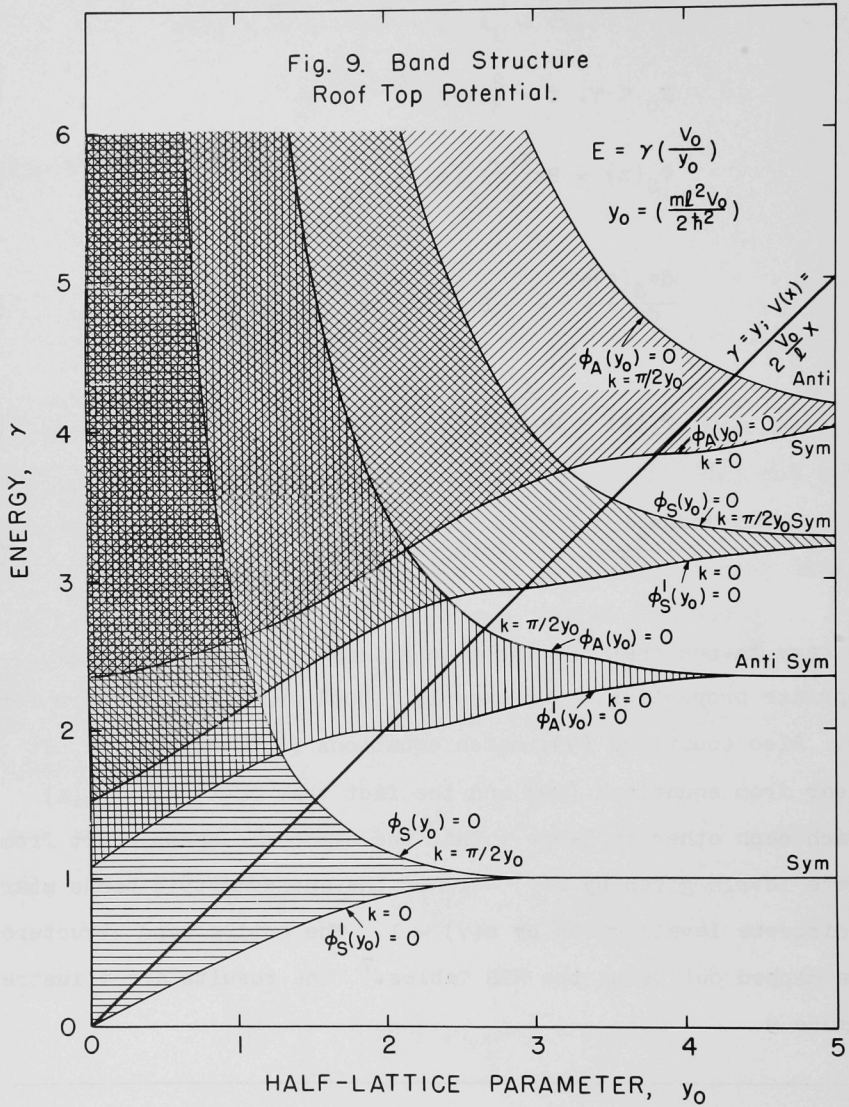
11. Three-Dimensional Periodic Potential Problems.

Let us consider problems for which

$$\frac{-\hbar^2}{2m} \nabla^2 \psi + \left\{ V(\overline{r}) - E \right\} \psi = 0, \tag{101a}$$

$$V(\overline{r} + \overline{l}) = V(\overline{r}), \tag{101b}$$

$$S = \frac{\hbar}{2im} (\psi^* \nabla \psi - \psi \nabla \psi^*), \tag{101c}$$

$$S(\overline{r} + \overline{l}) = S(\overline{r}). \tag{101d}$$

In an analogous fashion to the procedure followed in Section 4, let

$$\overline{P} = \frac{\nabla \psi}{\psi}, \tag{102}$$

where $\overline{P}$ is now a vector. Equation (101a) becomes

$$\nabla \cdot \overline{P} + \overline{P}^2 + \frac{2m}{\hbar^2} \left\{ E - V(\overline{r}) \right\} = 0, \tag{103a}$$

$$\overline{P}_I = \frac{\overline{P} - \overline{P}^*}{2i} = \frac{\hbar}{m} \frac{S}{|\psi|^2} \tag{103b}$$

$$\overline{P}_R = \frac{1}{2} \frac{\nabla |\psi|^2}{|\psi|^2}, \tag{103c}$$

$$\overline{P} = \frac{1}{2} \frac{\nabla |\psi|^2}{|\psi|^2} + \frac{i\hbar}{m} \frac{S}{|\psi|^2}. \tag{103d}$$

Since S and $|\psi|^2$ are periodic with the periods of the lattice, the vector $\overline{P}$ is also periodic.

Let us confine our attention to potentials $V(\overline{r}) \equiv V(x,y,z)$ which are separable:

$$V(x,y,z) = V_1(x) + V_2(y) + V_3(z). \tag{104}$$

Equation (103a) becomes

$$
\left.\begin{aligned}
&\frac{\partial P_x}{\partial x} + P_x^2 + \frac{2m}{h^2} E_x - \frac{2m}{h^2} V_1(x) \\[2mm]
&+ \frac{\partial P_y}{\partial y} + P_y^2 + \frac{2m}{h^2} E_y - \frac{2m}{h^2} V_2(y) \\[2mm]
&+ \frac{\partial P_z}{\partial y} + P_z^2 + \frac{2m}{h^2} E_z - \frac{2m}{h^2} V_3(z) = 0,
\end{aligned}\right\}
\tag{105a}
$$

$$
E_x + E_y + E_z = E. \tag{105b}
$$

For these separable potentials a particular solution $\overline{F}$ can be found such that

$$
\nabla \cdot \overline{F} + \overline{F}^2 + \frac{2m}{h^2}(E-V) = 0, \tag{106a}
$$

$$
\overline{F} = i F_x(x) + j F_y(y) + k F_z(z), \tag{106b}
$$

for under this latter circumstance equation (105a) is separable. As before we now attempt to use the particular solution $\overline{F}$ to linearize (103a):

$$
\overline{P} = \overline{F} + \overline{U}, \tag{107a}
$$

$$
\nabla \cdot \overline{P} = \nabla \cdot \overline{F} + \nabla \cdot \overline{U}, \tag{107b}
$$

$$
\overline{P}^2 = \overline{F}^2 + 2\overline{F} \cdot \overline{U} + \overline{U}^2, \tag{107c}
$$

$$
\nabla \cdot \overline{U} + 2\overline{F} \cdot \overline{U} + \overline{U}^2 = 0. \tag{107d}
$$

Further, we can write

$$
\nabla \cdot \left(e^{2\int_0^{\overline{r}} \overline{F} \cdot d\overline{s}} \overline{U} \right) = e^{2\int_0^{\overline{r}} \overline{F} \cdot d\overline{s}} (\nabla \cdot \overline{U} + 2\overline{F} \cdot \overline{U}), \tag{108a}
$$

$$\nabla \cdot (e^{2\phi}\overline{U}) = -U^2 e^{2\phi}, \tag{108b}$$

$$\phi = \int_0^{\overline{r}} \overline{F} \cdot d\overline{s} = \int_0^x F_x dx + \int_0^y F_y dy + \int_0^z F_z dz. \tag{108c}$$

Hence (108b) becomes

$$\nabla \cdot (e^{2\phi}\overline{U}) = -(\overline{U}e^{2\phi} \cdot \overline{U}e^{2\phi})e^{-2\phi}, \tag{109a}$$

$$\nabla \cdot \overline{T} = -T^2 e^{-2\phi}, \tag{109b}$$

$$\overline{T} = e^{2\phi}\overline{U}. \tag{109c}$$

A general solution to (109b) can be found by analogy with the one-dimensional case. Since our particular solution $\overline{F}$, has the form (106b) we can write

$$\phi_x = \int_0^x F_x dx; \quad \phi_y = \int_0^y F_y dy; \quad \phi_z = \int_0^z F_z dz, \tag{110a}$$

$$\phi = \phi_x + \phi_y + \phi_z. \tag{111}$$

The general solution to (109b) is:

$$\overline{T} = \frac{i}{f_1(y,z) + I_1} + \frac{j}{f_2(x,z) + I_2} + \frac{k}{f_3(x,y) + I_3}, \tag{112a}$$

where f_1, f_2, and f_3 are perfectly arbitrary functions, real or complex, of the indicated variables and

$$I_1 = \int_0^x e^{-2\phi} dx = e^{-2\phi_y} e^{-2\phi_z} \int_0^x e^{-2\phi_x} dx, \tag{112b}$$

$$I_2 = \int_0^y e^{-2\phi} dy = e^{-2\phi_x} e^{-2\phi_z} \int_0^y e^{-2\phi_y} dy, \tag{112c}$$

$$I_3 = \int_0^z e^{-2\phi} dz = e^{-2\phi_x} e^{-2\phi_y} \int_0^z e^{-2\phi_z} dz. \tag{112d}$$

The general solution to (106a) now becomes

$$\overline{P} = \overline{F} + e^{-2\phi}[\frac{i}{I_1 + f_1} + \frac{j}{I_2 + f_2} + \frac{k}{I_3 + f_3}]. \tag{113}$$

In analogy with our previous treatment of the one-dimensional problems, if $V_1(x)$, $V_2(y)$ and $V_3(z)$ are all even functions about $x = 0$, $y = 0$, $z = 0$, respectively, then F_x, F_y, and F_z can be chosen to be odd real functions of x, y, z respectively. Also the integrals I_1, I_2, and I_3 are all real quantities.

The remainder of the procedure can best be illustrated by application to a simple cubic lattice of half lattice period $\underline{a}$. We consider the origin of coordinates to be at the center of the cubic cells. The potential in each cell $V(x,y,z)$ is assumed to be separable, isotropic, and with reflection planes at $x = 0$, $y = 0$, $z = 0$. For this case we have the periodicity relations illustrated by the equation

$$P_x(a,y,z) = P_x(-a,y,z). \tag{114}$$

This relation and the symmetry property of $F_x(x)$ leads to the relation:

$$\left\{f_1(y,z)\right\}^2 = \frac{I_1(a)\left\{I_1(a)F_x(a) + e^{-2\phi_x(a)}e^{-2\phi_y(y)}e^{-2\phi_z(z)}\right\}}{F_x(a)} \tag{115}$$

where

$$I_1(a) = \int_0^a e^{-2\phi}dx = e^{-2\phi_y}e^{-2\phi_z}\int_0^a e^{-2\phi_x}dx. \tag{116}$$

Similar relations follow for $f_2(x,z)$ and $f_3(x,y)$. Thus the f_i are either real or pure imaginary since all the quantities in (115) are real. Let us assume now that $|\psi(\overline{r})|^2$ is invariant under the reflection symmetry operation. Exceptional cases may arise just as in the one-dimensional problems. However, as was true there,

the possible exceptions to the invariance of $|\psi(\overline{r})|^2$ under a reflection symmetry operation will be apparent in the final band structure as limiting cases of the normal situation where $|\psi(\overline{r})|^2$ is invariant. Just as in the one-dimensional case, this symmetry property allows us to conclude that the only real values of f_i are zero. Hence the allowed energy regions are given by the inequalities (the I_i are all positive)

$$\frac{I_x(a)F_x(a) + e^{-2\phi_x(a)}}{F_x(a)} \leqslant 0, \tag{117a}$$

$$\frac{I_y(a)F_y(a) + e^{-2\phi_y(a)}}{F_y(a)} \leqslant 0, \tag{117b}$$

$$\frac{I_z(a)F_z(a) + e^{-2\phi_z(a)}}{F_z(a)} \leqslant 0, \tag{117c}$$

where

$$I_x(a) = \int_0^a e^{-2\phi_x} dx, \tag{117d}$$

$$I_y(a) = \int_0^a e^{-2\phi_y} dy, \tag{117e}$$

$$I_z(a) = \int_0^a e^{-2\phi_z} dz. \tag{117f}$$

Thus $F_x(a)$, $F_y(a)$ and $F_z(a)$ must all be negative for any allowed solutions. However, negativity is not enough except that it is clear that as all the $F(a)$ go from positive to negative we will go from a forbidden region into an allowed region. Furthermore the $F(a)$ can change sign by an infinite discontinuity making it necessary to use symmetric and antisymmetric functions such as the following

$$F_x(E_x-E_{xo},x) = \phi'_S/\phi_S, \qquad (118a)$$

$$\phi_S \, I_x(x) = \phi_A, \qquad (118b)$$

where $\phi_S(E_x-E_{xo},x)$ is the symmetrical solution (see Section 9) and $\phi_A(E_x-E_{xo},x)$ is the antisymmetrical solution of the Schroedinger equation,

$$\psi''(x) + E \, \frac{2m}{\hbar^2} \, (E_x-E_{xo}-V_x)\psi(x). \qquad (119)$$

This requirement in the procedure is no more complicated than in the one-dimensional problem and will not be retreated here.

From equations (105a) we see that $F_x(a)$ will be a function of $E_x - E_{xo}$ where E_{xo} is a separation parameter involved in the solution of (105a) to get F_x. Similarly for F_y and F_z. For a given lattice parameter $2a$, $F_x(a)$, $F_y(a)$ and $F_z(a)$ will have zeros or changes in sign through infinite discontinuities. Let one such set of zeros take place when

$$E_x - E_{xo} = q_x, \qquad (120a)$$

$$E_y - E_{yo} = q_y, \qquad (120b)$$

$$E_z - E_{zo} = q_z. \qquad (120c)$$

The sum of these three equations gives

$$E = E_x + E_y + E_z = q_x + q_y + q_z, \qquad (121)$$

since the sum of the separation parameters is zero. Thus by examining the values of the energy parameters which satisfy inequalities (117) - actually their counter parts in terms of the symmetrical and antisymmetrical solutions of the separated Schroedinger equation - we can map out the entire band system as

a function of the lattice parameter or other parameters. $F_x(a, E_x-E_{xo})$, $F_y(a, E_y-E_{yo})$, and $F_z(a, E_z-E_{zo})$ all have exactly the same form, namely that for $f_o(y_o, \gamma)$ already discussed in Section 9 for the corresponding one-dimensional problem. Thus the extension to the three dimensional simple cubic lattice case is more or less trivial for all isotropic separable potentials with reflection symmetry once the one-dimensional problem is solved.

12. Concluding Remarks

The method used here should be examined with respect to its application to non-cubic lattices and perhaps also for potentials which do not have reflection symmetry. The latter could be done for a one-dimensional saw tooth potential and the results compared with those obtained by Sugiyama[8] for a finite chain of saw-teeth with infinite potentials at the end of the chain.

The author feels that the method described also has many pedagogical advantages. For example, the one-dimensional parabolic scallop potential is simpler than the Kronig-Penny potential well in that discontinuities and concomitant matching difficulties do not arise within the cell itself. The periodicity condition alone takes care of matching at the cusps of the potential at the cell wall. Also the behavior of the band system as a function of the period is more easily brought out in the parabolic scallop potential as is the symmetry properties of the eigenfunctions. The method also gets down to the fundamental essentials of the matching process and thus decreases the complexity of the algebra over that used in conventional procedures.

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[8]Yoshiyuhi Sugiyama, Research Reports, Memoirs of the Faculty of Engineering, Nagoya University, Vol. 12, No. 1, May 1960, pp. 64-72.

Acknowledgment

APPENDIX I

Theorem III:

The relation

$$\psi_k(\bar{r}) = u_k(\bar{r}) \, e^{i\bar{k}\cdot\bar{r}} \tag{1}$$

follows from the two conditions:

$$|\psi(\bar{r} + \bar{l})|^2 = |\psi(\bar{r})|^2 \quad , \tag{2a}$$

$$\bar{S}(\bar{r} + \bar{l}) = \bar{S}(\bar{r}) \quad . \tag{2b}$$

Since the validity of equation (1) clearly implies the validity of equations (2a) and (2b) (See page 5, text), proof of the above Theorem establishes the complete equivalence of the Bloch condition (1) and equations (2) as criteria for the selection of appropriately well-behaved eigenfunctions.

Proof: Since $\psi(\bar{r})$ is complex in general, we may write it as follows:

$$\psi(\bar{r}) = R(\bar{r}) + iI(\bar{r}) = + \sqrt{R^2 + I^2} \, e^{i\tan^{-1}I/R} \quad , \tag{3}$$

$$\psi(\bar{r}) = f(\bar{r}) \, e^{ig(\bar{r})} \quad ,$$

where $f(\bar{r})$ and $g(\bar{r})$ are real scalar functions of the position coordinates $\bar{r} = (x, y, z)$ and where $f(\bar{r})$ is restricted without loss of generality to non-negative values by the choice of the positive square root. For a periodic potential, $V(\bar{r})$, the following equations must hold:

$$V(\bar{r}) = V(\bar{r} + \bar{l}) \quad , \tag{4}$$

$$\frac{-\hbar^2}{2m} \nabla^2 \psi(\bar{r}) + \left\{V(\bar{r})-E\right\} \psi(\bar{r}) = 0 \qquad , \qquad (5)$$

$$\frac{-\hbar^2}{2m} \nabla^2 \psi(\bar{r} + \bar{l}) + \left\{V(\bar{r})-E\right\} \psi(\bar{r} + \bar{l}) = 0 \qquad . \qquad (6)$$

Because of the periodicity (2a) on the position probability density, it is immediately obvious that $f(\bar{r})$ is periodic: Thus

$$\psi^*(\bar{r}) \ \psi(\bar{r}) = \psi^*(\bar{r} + \bar{l}) \ \psi(\bar{r} + \bar{l}) \qquad ,$$

$$[f(\bar{r})]^2 = [f(\bar{r} + \bar{l})]^2 \qquad ,$$

and finally, since $f(\bar{r})$ is non-negative and real everywhere,

$$f(\bar{r} + \bar{l}) = f(\bar{r}) \qquad . \qquad (7)$$

Also upon applying the periodicity condition (2b) on $\bar{S}$ to (3) we have

$$S = \frac{\hbar}{2im} \ 2if^2 \ \nabla g = \frac{\hbar}{m} \ f^2 \nabla g \qquad , \qquad (8)$$

$$\nabla g(\bar{r} + \ell) = \nabla g(\bar{r}) \qquad . \qquad (9)$$

Equation (9) has only one solution

$$g(\bar{r} + \bar{l}) - g(\bar{r}) = C_\ell \qquad , \qquad (10)$$

where C_ℓ is a constant appropriate for the direction $\bar{l}$. We can further assume $\bar{l}$ to be the shortest lattice vector in the direction $\bar{l}$. Hence we have shown that <u>the phase of $\psi(\bar{r})$ advances by a constant amount C_ℓ, independent of position in the lattice, when one goes from equivalent point to equivalent point along any given lattice direction.</u>

C_ℓ may be restricted to the interval $0 \leqslant C_\ell < 2\pi$ or any equivalent interval. Let us take the components of the lattice vector $\bar{l}$ to be (ℓ_x, ℓ_y, ℓ_z); then

$$g(x+\ell_x,\ y+\ell_y,\ z+\ell_z) = g(x,y,z) + C(\ell_x, \ell_y, \ell_z) \qquad , \qquad (11)$$

where C is independent of x,y,z but depends on direction components $\ell_x,\ \ell_y,\ \ell_z$.

A general solution for $g(x,y,z)$ which satisfies equation (11) is the following:

$$g(x,y,z) = P(x,y,z;\ \ell_x, \ell_y, \ell_z) + \frac{C_x}{\ell_x}\, x + \frac{C_y}{\ell_y}\, y + \frac{C_z}{\ell_z}\, z \qquad , \qquad (12)$$

where $P(x,y,z;\ \ell_x, \ell_y, \ell_z)$ is <u>any</u> periodic function of x,y,z with periods $\ell_x,\ \ell_y,$ and ℓ_z respectively, and where

$$C_x + C_y + C_z = C(\ell_x, \ell_y, \ell_z) \qquad . \qquad (13)$$

For the purposes of getting a general solution of (11), $P(x,y,z)$ can be regarded as a perfectly general periodic function; however, it must be restricted to a particular function if $\psi(\bar{r}) = f(r)\, e^{ig(\bar{r})}$ is to satisfy the Schroedinger equation (5). From (12) and (13) it follows that

$$\psi(\bar{r}) = f(\bar{r})\, e^{iP(\bar{r})}\, e^{i(C_x \frac{x}{\ell_x} + C_y \frac{y}{\ell_y} + C_z \frac{z}{\ell_z})} \qquad , \qquad (14)$$

$$\psi(\bar{r}) = f(\bar{r})\, e^{iP(\bar{r})}\, e^{i\bar{k}\cdot\bar{r}} = u_k(\bar{r})\, e^{i\bar{k}\cdot r} \qquad , \qquad (15)$$

where

$$\bar{k} = (\frac{C_x}{\ell_x}, \frac{C_y}{\ell_y}, \frac{C_z}{\ell_z}) \tag{16}$$

must satisfy the condition

$$k_x \ell_x + k_y \ell_y + k_z \ell_z = \bar{k} \cdot \bar{\ell} = C_\ell \tag{17}$$

but is otherwise arbitrary. Since $f(\bar{r})\, e^{iP(\bar{r})}$ is periodic, and since the choice of the particular lattice vector $\bar{\ell}$ was perfectly arbitrary, we have proven the theorem. Hence we may use either

$$|\psi(\bar{r} + \bar{\ell})|^2 = |\psi(\bar{r})|^2 \text{ and } \bar{S}(\bar{r} + \bar{\ell}) = S(\bar{r}) \quad , \tag{18}$$

or

$$\psi(\bar{r}, E) = u_k(\bar{r})\, e^{i\bar{k}\cdot\bar{r}} \; ; \; u_k(\bar{r} + \bar{\ell}) = u_k(\bar{r}) \tag{19}$$

interchangeably as the criteria for selection of physically suitable eigenfunctions.

For one-dimensional problems, $\nabla \cdot \bar{S} = 0$, $\bar{S} = S(x) = \text{constant}$; hence $\bar{S}(\bar{r} + \bar{\ell}) = \bar{S}(\bar{r})$ is automatically fulfilled for __all__ solutions of the Schroedinger equation. In this case $|\psi(x + \ell)|^2 = |\psi(x)|^2$ is both a necessary and a sufficient condition for the selection of the "well-behaved" solutions. That is, the condition of periodicity of $|\psi(x)|^2$ is completely equivalent to the Bloch condition.

APPENDIX II

__Theorem IV__: The criterion, $|\psi(x + \ell)|^2 = |\psi(x)|^2$, for physically acceptable solutions of the Schroedinger equation

$$-\frac{\hbar^2}{2m} \psi'' + (V - E) \psi = 0, \tag{1}$$

where

$$V(x+\ell) = V(x), \; V(x) = V(-x), \tag{2}$$

leads to the relation

$$|\psi(x)|^2 = |\psi(-x)|^2, \tag{3}$$

except for the special case for which there are two equally good real solutions; one antisymmetric and one symmetric, $\psi_1(x)$ and $\psi_2(x)$ respectively, such that

$$\psi_1(x+\ell) = \alpha\psi_1(x),$$

$$\psi_2(x+\ell) = \alpha\psi_2(x), \tag{4}$$

$$\alpha = \pm 1.$$

Proof of Theorem: The second order differential equation (1) has two independent solutions. Let us choose two particular solutions $\psi_1(x)$ and $\psi_2(x)$ such that they obey the following initial conditions:

$$\psi_1(0) = 0; \; \psi_1'(0) = 1,$$

$$\psi_2(0) = 1; \; \psi_2'(0) = 0. \tag{5}$$

Since V(x) is a real function and since the energy and the other parameters and constants occurring in (1) are real, the above initial conditions insure that $\psi_1(x)$ and $\psi_2(x)$ are both real functions. Furthermore $\psi_1(x)$ is an odd function and $\psi_2(x)$ is even. This follows from the evenness of V(x). Hence,

$$\psi_1(-x) = -\psi_1(x),$$

$$\psi_2(-x) = \psi_2(x). \tag{6}$$

Now $\psi_1(x+\ell)$ and $\psi_2(x+\ell)$ are also solutions of (1) because of the relation $V(x+\ell) = V(x)$. Since there are only two independent solutions we must have

$$\psi_1(x+\ell) = \alpha_1 \psi_1(x) + \alpha_2 \psi_2(x),$$
$$\psi_2(x+\ell) = \beta_1 \psi_1(x) + \beta_2 \psi_2(x). \tag{7}$$

$\psi_1(x)$, $\psi_2(x)$ and hence $\psi_1(x+\ell)$ and $\psi_2(x+\ell)$ are all real; the constants α_1, α_2, β_1 and β_2, <u>which must have very particular values for each eigenvalue E</u>, are also all real numbers. This follows from the linear independence of $\psi_1(x)$ and $\psi_2(x)$, since $\alpha_{1I}\psi_1(x) + \alpha_{2I}\psi_2(x)$ and $\beta_{1I}\psi_1(x) + \beta_{2I}\psi_2(x)$, the imaginary parts of the right sides of equations (7), can be zero only if the α's and β's are real.

Let $x \to -x$ in equations (7) and use the symmetry properties of ψ_1 and ψ_2. Thus we obtain

$$\psi_1(-x+\ell) = -\psi_1(x-\ell) = -\alpha_1\psi_1(x) + \alpha_2\psi_2(x),$$
$$\psi_2(-x+\ell) = \psi_2(x-\ell) = -\beta_1\psi_1(x) + \beta_2\psi_2(x), \tag{8}$$

Now let $x \to x+\ell$ in equations (8) and use equations (7). We obtain the following equations:

$$-\psi_1(x) = -\alpha_1[\alpha_1\psi_1(x) + \alpha_2\psi_2(x)] + \alpha_2[\beta_1\psi_1(x) + \beta_2\psi_2(x)],$$
$$\psi_2(x) = -\beta_1[\alpha_1\psi_1(x) + \alpha_2\psi_2(x)] + \beta_2[\beta_1\psi_1(x) + \beta_2\psi_2(x)], \tag{9}$$

and, since $\psi_1(x)$ and $\psi_2(x)$ are linearly independent,

$$-1 = -\alpha_1^2 + \alpha_2\beta_1 \; ; \; 0 = -\alpha_1\alpha_2 + \alpha_2\beta_2,$$
$$1 = -\beta_1\alpha_2 + \beta_2^2 \; ; \; 0 = -\beta_1\alpha_1 + \beta_2\beta_1. \tag{10}$$

A general solution of the wave equation is given by

$$\psi(x) = A\psi_1(x) + B\psi_2(x), \tag{11}$$

where A and B are arbitrary constants, real or complex. Also

$$\psi(x+\ell) = A\psi_1(x+\ell) + B\psi_2(x+\ell),$$

$$\psi(x+\ell) = (A\alpha_1+B\beta_2)\ \psi_1(x) + (A\alpha_2+B\beta_2)\ \psi_2(x). \tag{12}$$

The particular linear combinations we are seeking must satisfy
the following equations:

$$|\psi(x+\ell)|^2 = |\psi(x)|^2 , \tag{13a}$$

$$|(A\alpha_1+B\beta_1)\ \psi_1(x) + (A\alpha_2+B\beta_2)\ \psi_2(x)|^2 = |A\psi_1(x) + B\psi_2(x)|^2, \tag{13b}$$

$$
\left.
\begin{aligned}
&\psi_1^2(x)[AA^*\alpha_1^2 + (AB^*+A^*B)\ \alpha_1\beta_1 + BB^*\beta_1^2] \\
&\qquad + \\
&\psi_1(x)\psi_2(x)[AA^*2\alpha_1\alpha_2 + (AB^*+A^*B)(\alpha_1\beta_2+\alpha_2\beta_1)+BB^*2\beta_1\beta_2] \\
&\qquad + \\
&\psi_2^2(x)[AA^*\alpha_2^2 + (AB^*+A^*B)\alpha_2\beta_2 + BB^*\beta_2^2]
\end{aligned}
\right\}
=
\begin{aligned}
&\psi_1^2(x)\ AA^* \quad (13c) \\
&\qquad + \\
&\psi_1(x)\psi_2(x)(AB^*+A^*B) \\
&\qquad + \\
&\psi_2^2(x)\ BB^*.
\end{aligned}
$$

From the fact that $\psi_1(o) = 0$ and $\psi_2(o) = 1$, we conclude immediately
the the coefficients of $\psi_2^2(x)$ must be equal on the right and
left sides of the last equation, and then because of the inde-
pendence of $\psi_1(x)$ and $\psi_2(x)$ the coefficients of $\psi_1^2(x)$ and of
$\psi_1(x)\psi_2(x)$ must also be equal on both sides. Hence we have the
relations which the A and B must satisfy in terms of the α's and
β's; the latter, of course, are determined by the form of the po-
tential and by the energy E:

$$AA^*(\alpha_1^2-1) + (AB^*+A^*B)\alpha_1\beta_1 + BB^*\beta_1^2 = 0, \tag{14a}$$

$$AA^*2\alpha_1\alpha_2 + (AB^*+A^*B)(\alpha_1\beta_2+\alpha_2\beta_1-1) + BB^*2\beta_1\beta_2 = 0, \tag{14b}$$

$$AA^*\alpha_2^2 + (AB^*+A^*B)\ \alpha_2\beta_2 + BB^*(\beta_2^2-1) = 0. \tag{14c}$$

If no linear combination of $\psi_1(x,E)$ and $\psi_2(x,E)$ exists which satisfies (13a) other than that for which A=B=0, then $\underline{E}$ is not an allowed energy of the system. If, however, combinations exist satisfying (13a) for which one or both of the constants A and B are not zero, then $\underline{E}$ is an allowed energy.

Using equations (10) we may rewrite equations (14) as follows:

$$AA^*\alpha_2\beta_1 + (AB^*+A^*B)\,\alpha_1\beta_1 + BB^*\beta_1^{\,2} = 0 \qquad , \quad (15a)$$

$$AA^*2\alpha_1\alpha_2 + (AB^*+A^*B)(\alpha_1\beta_2+\alpha_2\beta_1-1) + BB^*2\beta_1\beta_2 = 0 \,, \quad (15b)$$

$$AA^*\alpha_2^{\,2} + (AB^*+A^*B)\,\alpha_2\beta_2 + BB^*\alpha_2\beta_1 = 0 \qquad . \quad (15c)$$

Clearly, if an exception exists such that

$$|\psi(x)|^2 \neq |\psi(-x)|^2 \qquad\qquad , \quad (16)$$

then $AB^* + A^*B \neq 0$, since

$$|\psi(x)|^2 = AA^*\psi_1^{\,2}(x) + (AB^*+A^*B)\psi_1(x)\psi_2(x) + BB^*\psi_2^{\,2}(x) \,,$$

and

$$|\psi(-x)|^2 = AA^*\psi_1^{\,2}(x) - (AB^*+A^*B)\psi_1(x)\psi_2(x) + BB^*\psi_2^{\,2}(x).$$

Hence, neither A nor B can be zero. That is, none of the constants AA^*, AB^*+A^*B, BB^* in equations (15) can be zero. The only set of values of α_1,α_2, β_1, β_2 which is possible with this limitation and those contained in equations (10) is:

$$\alpha_1 = \beta_2 = \alpha = \pm 1 \,,$$
$$\alpha_2 = \beta_1 = 0 \qquad . \qquad\qquad (17)$$

Hence, whenever we have

$$\psi_1(x+\ell) = \alpha\psi_1(x) \,,$$
$$\psi_2(x+\ell) = \alpha\psi_2(x), \qquad\qquad (18)$$
$$\alpha = \pm 1 \,,$$

a completely general solution,

$$\psi(x+\ell) = A\psi_1(x) + B\psi_2(x), \tag{19}$$

satisfies the periodicity on the probability density

$$\psi(x+\ell) = \alpha\psi(x) \qquad ,$$

$$|(x+\ell)|^2 = |\psi(x)|^2 \qquad , \tag{20}$$

but for general A and B values the inequality holds in the relation

$$|\psi(-x)|^2 \neq |\psi(x)|^2 \qquad .$$

The exceptional case can occur only on the edge of a band since Wilson[2] has shown that the periodicity or antiperiodicity of the eigenfunction

$$\psi(x+\ell) = \alpha\psi(x) = \pm\,\psi(x) \tag{21}$$

holds only at the boundary separating allowed and forbidden energy bands.

APPENDIX III

Given the following relations:

$$\psi''(y) + \left\{ \gamma - V(y) \right\} \psi(y) = 0, \tag{1a}$$

$$V(y) = V(-y), \tag{1b}$$

$$V(y + 2y_0) = V(y); \tag{1c}$$

we wish to find the appropriate solutions $\psi(\gamma,y)$ which have the property that

$$|\psi(\gamma,y)|^2 = |\psi(\gamma,y + 2y_0)|^2. \tag{2a}$$

This may be written equally well in the form

$$\psi(\gamma,y + 2y_0) = e^{i\theta} \psi(\gamma,y). \tag{2b}$$

In Appendix I it is shown that θ is independent of y.

Also, in order to have physically meaningful solutions, the logarithmic derivative $\psi'(y)/\psi(y)$ must match across all discontinuities in $V(y)$ or its derivatives and it must be periodic with the period of the lattice. Hence

$$\frac{\psi'(\gamma,y)}{\psi(\gamma,y)} = \frac{\psi'(\gamma,y + 2y_0)}{\psi(\gamma,y + 2y_0)}. \tag{3}$$

Let the general solution of (1a) be written as a linear combination of a symmetrical solution, ϕ_S, and an antisymmetrical solution ϕ_A, where

$$\phi_S(\gamma,o) = 1; \quad \phi_{S'}(\gamma,o) = 0, \tag{4a}$$

$$\phi_A(\gamma,o) = 0; \quad \phi_{A'}(\gamma,o) = 1, \tag{4b}$$

$$\psi(\gamma,y) = A\phi_S(\gamma,y) + B\phi_A(\gamma,y). \tag{4c}$$

Independent solutions of the form of ϕ_S and ϕ_A always exist for even potentials $V(y)$. The solution (4c) is assumed to be valid

in the region $\left\{-y_0 + 0, + y_0 - 0\right\}$. If there are any discontin-uities or lack of smoothness in $V(y)$ inside the region $\left\{-y_0, y_0\right\}$ we assume that the piecewise solutions have been matched across the discontinuities to give (4c). We now impose conditions (2b) and (3) at the point $y = (-y_0 + 0)$ to equation (4c).

Application of (2b) leads immediately to the following re-lations:

$$\psi(y_0 + 0) = e^{i\theta_1}\psi(-y_0 + 0), \tag{5a}$$

$$\psi(y_0 + 0) = e^{i\theta_2}\psi(y_0 - 0), \tag{5b}$$

$$\psi(y_0 - 0) = e^{i(\theta_1 - \theta_2)}\psi(-y_0 + 0) = e^{i\theta_0}\psi(-y_0 + 0), \tag{5c}$$

$$e^{i\theta_0}\left\{A\phi_S(y_0) - B\phi_A(y_0)\right\} = \left\{A\phi_S(y_0) + B\phi_A(y_0)\right\}, \tag{5d}$$

$$A\phi_S(y_0)\left\{e^{i\theta_0} - 1\right\} = B\phi_A(y_0)\left\{1 + e^{i\theta_0}\right\}, \tag{5e}$$

$$+ i A \sin\theta_0/2 \ \phi_S(y_0) = B \cos \theta_0/2 \ \phi_A(y_0). \tag{5f}$$

Equation (5b) is necessary because the value of the eigenfunction just inside the next cell to the right of $y = y_0$ is not necessar-ily the same as the value of the eigenfunction immediately to the left of $y = y_0$. For a discussion of this point refer back to Section 5, Equation 31a.

Application of condition (3) gives

$$\left.\frac{A\phi_S' + B\phi_A'}{A\phi_S + B\phi_A}\right|_{-y_0} = \left.\frac{A\phi_S' + B\phi_A'}{A\phi_S + B\phi_A}\right|_{+y_0}, \tag{6a}$$

$$A^2\phi_S(y_0)\phi_S'(y_0) = B^2\phi_A(y_0)\phi_A'(y_0). \tag{6b}$$

We now consider the possible cases separately where either A or B is zero (obviously both cannot be zero) and where neither is

zero.

$$A = 0, B \neq 0$$

$$\psi(y) = B\phi_A(y) \text{ in } \left\{-y_o +0, y_o -0\right\}$$

In this case B can be taken to be real in the sample interval centered on $y = 0$. From this it follows that ψ is real everywhere (ψ real over a finite interval can never become complex). Hence θ_1, $\theta_2 = 0$ or π. Since $\phi_A(y)$ is odd, $\theta_o = \pi$. It follows that (5f) is automatically satisfied while (6b) requires either $\phi_A(y_o) = 0$ or $\phi_A'(y_o) = 0$. Thus we have:

$$\phi_A(y_o-0) = 0 \qquad\qquad \phi_A'(y_o-0) = 0$$
$$\phi_A'(y_o-0) \neq 0 \qquad\qquad \phi_A(y_o-0) \neq 0$$
$$\phi_A(y_o+0) = 0 \qquad\qquad \phi_A'(y_o+0) = 0$$
$$\phi_A'(y_o+0) = \pm\, \phi_A'(y_o-0). \qquad \phi_A(y_o+0) = \pm\, \phi_A(y_o-0).$$

Hence $\psi(y+2y_o)$ looks just like $\psi(y)$ or _is its negative_. Hence $\psi(y)$ is an odd periodic function about $y = 0$ and about the other reflection symmetry points $\pm\, n2y_o$ with period $2y_o$ or $4y_o$. That is to say, $\psi(y) = B\phi_A(y)$ is either a real periodic or a real antiperiodic function.

An exactly similar situation arises for the case where $A \neq 0$, $B = 0$. Here the eigenfunction is an even periodic function, $\psi(y) = A\phi_S(y)$, with either $\phi_S(y_o) = 0$ or $\phi_S'(y_o) = 0$; θ_1, $\theta_2 = 0$ or π and $\theta_o = 0$. Ignoring the possible shift of phase of $\theta_2 = \pi$, which has no physically observable consequencies, in going from one cell to the next the solution $\phi_S(y_o) = 0$ corresponds to an antiperiodic symmetrical solution (period $4y_o$) and $\phi_S'(y_o)$ corresponds to a periodic symmetrical solution.

Now consider the case where neither A nor B is equal to zero. From (6b) we see that A^2/B^2 is real; hence A/B is real or pure imaginary.

First let

$$A/B = i\ C; \tag{7a}$$

then

$$- C^2 = \frac{\phi_A(y_o)\ \phi_A'(y_o)}{\phi_S(y_o)\ \phi_S'(y_o)} < 0, \tag{7b}$$

where C is real and cannot be zero or infinity. Hence

$$- \infty < \frac{\phi_A(y_o)\ \phi_A'(y_o)}{\phi_S(y_o)\ \phi_S'(y_o)} < 0. \tag{8}$$

There are two possibilities in relation (8): (1) none of the terms are zero and (2) the pairs $\phi_A(y)$, $\phi_S'(y)$ and $\phi_A'(y)$, $\phi_S(y)$ go to zero together as y approaches y_o. For the latter cases we have

$$\frac{\phi_A'(y_o)}{\phi_S(y_o)} \underset{y \to y_o}{\text{L}} \frac{\phi_A(y)}{\phi_S'(y)} = \frac{[\phi_A'(y_o)]^2}{[\phi_S(y_o)]^2} \frac{1}{\{V(y_o)-\gamma\}}, \tag{9a}$$

and

$$\frac{\phi_A(y_o)}{\phi_S'(y_o)} \underset{y \to y_o}{\text{L}} \frac{\phi_A'(y)}{\phi_S(y)} = \frac{[\phi_A(y_o)]^2\{V(y_o)-\gamma\}}{[\phi_S'(y_o)]^2}. \tag{9b}$$

For these exceptional cases of juxtaposition of zeros to occur when A/B is pure imaginary it is necessary that $\gamma \geqslant V(y_o)$. Also when $\phi_A(y_o) = 0$ we see from (5f) that $\theta_o = 0$. [$\phi_S(y_o)$ and $\phi_A(y_o)$ cannot be simultaneously zero otherwise the Wronskian

$$W = \phi_S\phi_A' - \phi_S'\phi_A = 1 \tag{10}$$

would not be constant.] Hence both $\phi_S(y)$ and $\phi_A(y)$ are periodic again ignoring the possible phase shift across y_o, and

$$\psi(y) = B(i \; C \; \phi_S + \phi_A) \tag{11a}$$

$$\psi(-y) = B(i \; C \; \phi_S - \phi_A) \tag{11b}$$

$$|\psi(y)|^2 = |B|^2[C^2 \; \phi_S^2 + \phi_A^2] = |\psi(-y)|^2 \tag{11c}$$

When both $\phi_S(y_o)$ and $\phi_A'(y_o)$ are zero, $\theta_o = \pi$, and both $\phi_S(y)$ and $\phi_A'(y)$ are antiperiodic. As before $|\psi(y)|^2 = |\psi(-y)|^2$.

Finally we examine the case when A and B are not zero but have a real ratio. From (5f) we see that either $\phi_A(y_o) = 0$ and $\theta_o = 0$, or $\phi_S(y_o) = 0$ and $\theta_o = \pi$. From (6b) we must also have $\phi_S'(y_o) = 0$ when $\phi_A(y_o) = 0$ and $\phi_A'(y_o) = 0$ when $\phi_S(y_o) = 0$. These pairs of zeros can occur for real A/B only when $\gamma \leqslant V(y_o)$. As before the solutions correspond to situations where both ϕ_S and ϕ_A are periodic or antiperiodic. <u>In these cases, and only in these cases, there is an exception to the evenness of $|\psi(y)|^2$ about the reflection symmetry points.</u>

In summary relation (8) may be generalized to include all cases discussed. The result is:

$$- \infty \leqslant \frac{\phi_A(y_o) \; \phi_A'(y_o)}{\phi_S(y_o) \; \phi_S'(y_o)} \leqslant 0. \tag{12}$$

The loci of all points of γ vs. y_o obtained from the equations:

$$\phi_A(\gamma,y_o) = 0; \; \phi_A'(\gamma,y_o) = 0; \; \phi_S(\gamma,y_o) = 0; \; \phi_S'(\gamma,y_o) = 0 \tag{13}$$

will give the boundaries of the allowed bands. The boundary curves $\phi_A(\gamma,y_o)$ and $\phi_S'(\gamma,y_o)$ may touch, coalesce, or intersect, and likewise the curves $\phi_S(\gamma,y_o)$ and $\phi_A'(\gamma,y_o)$. If they do this in a region for which $\gamma \leqslant V(y_o)$ then an exception may arise to the evenness of the probability density. The next paragraph further discusses this point. All other situations correspond to the inequalities in (12) and $|\psi(y)|^2$ is even.

The energy band structure of γ vs. y_o is a general property of the shape of the potential and should be independent of any linear translation of the coordinate y. Hence for all potentials such as those considered here where there is a lower bound a translation of the origin can be made such that y_o appears at the lower bound and all γ under consideration are greater than or equal to $V(y_o)$. If this translation does not destroy the reflection symmetry assumed for $V(y)$ then all our previous analysis holds and in this case if two boundary curves of γ vs. y_o cross or touch they will always do so within the limits of equation (7b) and $|\psi(y)|^2$ will be equal to $|\psi(-y)|^2$. It is clear that all of the potentials considered in this report fit the conditions outlined. Hence no exceptions to the evenness of $|\psi(y)|^2$ arise.

It is also useful to demonstrate the Bloch k value for our solutions. Let us eliminate A and B from equations (5f) and (6b). The result is

$$\sin^2 \frac{\theta_o}{2} = -\phi_A(y_o)\phi_S'(y_o).\tag{14}$$

Now from (5c) one notices that the phase advance of $\psi(y)$ in going from $-y_o$ to $+y_o$ is just $-\theta_o$. Since the phase advance per period is constant (see Appendix I), $-\theta_o$ is the phase advance per lattice period independent of position. From the Bloch equation the phase advance per unit length is k. Hence

$$-\theta_o = k2y_o,\tag{15}$$
$$\sin^2 ky_o = -\phi_A(y_o)\phi_S'(y_o).\tag{16}$$

When $\phi_A(y_o)$ or $\phi_S'(y_o)$ equals zero, $k = 0$, and when $\phi_S(y_o)$ or $\phi_A'(y_o)$ equals zero, $k = \frac{\pi}{2y_o}$.